



Demonstration of Nonanthropogenic Arsenic: Madison River, Madison County, Montana

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ACRONYMS

| | |
|---------|-------------------------------------------------|
| AAL | Anthropogenic Arsenic Load |
| CV | Coefficient of Variation |
| DEQ | Department of Environmental Quality |
| DON | Demonstration of Nonanthropogenic |
| EPA | Environmental Protection Agency |
| GIS | Geographical Information System |
| GW | Groundwater |
| GWIC | Groundwater Information Center |
| HUC | Hydrologic Unit Code |
| ICIS | Integrated Compliance Information System |
| kg/day | Kilograms per day |
| LOADEST | Load Estimator |
| LUST | Leaking Underground Storage Tank |
| MBMG | Montana Bureau of Mines and Geology |
| MCA | Montana Code Annotated |
| ML | Mass Load |
| MLE | Maximum Likelihood Estimation |
| NAL | Nonanthropogenic Arsenic Load |
| NLCD | National Land Cover Database |
| NRCS | National Resource Conservation Service |
| NWIS | National Water Information System |
| PSL | Point Source Load |
| PTRCB | Petroleum Tank Release Compensation Board |
| QAPP | Quality Assurance Project Plan |
| RO | Total Runoff |
| ROA | Runoff Anthropogenic |
| RRs | Remediation Response Sites |
| SAP | Sampling and Analysis Plan |
| STEPL | Spreadsheet Tool for Estimating Pollutant Loads |
| SWAT | Soil and Water Assessment Tool |
| t/yr | tons per year |
| TAL | Total Arsenic Load |
| TMDL | Total Maximum Daily Load |
| ug/L | microgram per liter |
| USFS | United States Forest Service |
| USGS | United States Geological Survey |
| USLE | Universal Soil Loss Equation |
| WQPB | Water Quality Planning Bureau |
| WQSM | Water Quality Standards and Modeling Section |
| YNP | Yellowstone National Park |

1.0 INTRODUCTION

This document presents the methods and results for the demonstration of nonanthropogenic (DON) arsenic for the Madison River Basin. The Madison River Basin includes the Madison River watershed from West Yellowstone to the mouth of the Madison River near Three Forks, Montana and all associated tributaries and drainages. For this demonstration, the terms natural and nonanthropogenic are synonymous and mean the background concentration of a parameter, in this case arsenic, due only to non-human induced sources. The Water Quality Standards and Modeling Section (WQSM) of the Montana Department of Environmental Quality's (DEQ) Water Quality Planning Bureau (WQP) has completed this demonstration.

Many figures within this document are not appropriate for grayscale and best viewed when printed in color.

1.1 PURPOSE

The purpose is to develop an arsenic standard for the Madison River that is based on natural conditions. A scientifically defensible DON is a first step in the process of developing standards based on a nonanthropogenic condition.

1.2 SUPPORTING DOCUMENTS

Investigations completed by the United States Geological Survey (USGS) and other researchers conclude that the likely sources of the elevated arsenic concentrations in the Madison River are from nonanthropogenic sources. The geothermal water of the Yellowstone Caldera in Yellowstone National Park (YNP) provides the largest source of arsenic loading to the Madison River and has been well documented by the following list of researchers. The complete citations are located in the reference section of this document.

- John D. Hem, 1985.
- David A. Nimick, Johnnie N. Moore, Charles E. Dalby, and Michael W. Savka, 1998.
- Jack J. Rowe, Robert O. Fournier, and G. W. Morey, 1973.
- L.K. Tuck, 2001
- L.K. Tuck, DeAnn. M. Dutton, and David. A. Nimick, 1997
- K.A. Miller, M. L. Clark, and P. R. Wright, 2004

The quality assurance descriptions for field data collection, data compilation and modeling described in this document were provided in the DEQ Quality Assurance Project Plan (QAPP) and Sampling and Analysis Plans (SAP) (DEQ, 2015a, 2015b, 2016b). Full citations are located in the reference section of this document.

1.3 BACKGROUND

In YNP, there are over 10,000 thermal features including more than 300 geysers (YNP, 2015). Many of these are located in the Firehole and Gibbon River basins, which join in the park to form the Madison River. The Madison River eventually joins the Jefferson and Gallatin Rivers near Three Forks, Montana to

form the headwaters of the Missouri River. A recent DEQ Madison River/Upper Missouri Water Quality Assessment and Total Maximum Daily Load (TMDL) project reported arsenic concentrations of samples collected from the Madison River above the Montana human health criterion of 10 µg/L (DEQ, 2016a, 2012). Per 2015 Senate Bill 325, codified as Montana Code Annotated (MCA) 75-5-222, DEQ may not apply a water quality standard to a water body that has a nonanthropogenic concentration greater than the standard (75-5-222, MCA). In this case, the standard would be set at the natural condition of the water body.

DEQ WQSM section conducted an investigation to characterize the level of natural arsenic loads in the Upper Missouri Basin. The specific objectives of the WQSM investigation are described in the project QAPP (DEQ, 2015a) and SAPs (DEQ, 2015b, 2016b). The results applicable to the DON are described in this document.

2.0 METHODS

The steps associated with the Madison River demonstration of nonanthropogenic (DON) arsenic are listed below:

- Define the Hydrologic Region (i.e., the study frame)
- Data Compilation
- Mass Load Analysis
- Mass Balance Approach

The specific methods for the DON steps are summarized in the following sections. The results of these steps are presented in **Section 4.0**.

2.1 HYDROLOGIC REGION

The first step was to define the hydrologic region of interest. The entire Madison River watershed is the area of interest for this study and is shown in **Figure 2-1**.

The United States Geological Survey (USGS) Hydrologic Unit Codes (HUCs) is a convenient way to classify watersheds. Using this system, the largest division for the Madison River hydrologic region was a HUC8 (8 digit code), followed by a HUC10 and then a HUC12. These categories progressively divide the basin into smaller sub-basins. The Madison River HUC8 code is 10020007 and defines the entire Madison River from Yellowstone National Park to the mouth of the Madison River near Three Forks. Smaller geographic regions within this HUC8 were recognized for modeling purposes. For example, there were 64 HUC12s within the Madison Basin (**Figure 2-1**).

Individual tributaries within the hydrologic region were defined as major or minor. The metric for determining whether a tributary was major differs depending on the basin. For the Madison River, a major tributary was defined as a percent of the total volume of the main river. For instance, a tributary volume contributing one percent to the overall volume of the main river was considered major. Major tributaries were determined based on their low flow volumes (defined as flows from August through April). The tributaries that were considered major had average low flow volumes greater than 5 percent of the median low flow volume of the Madison River at the mouth.

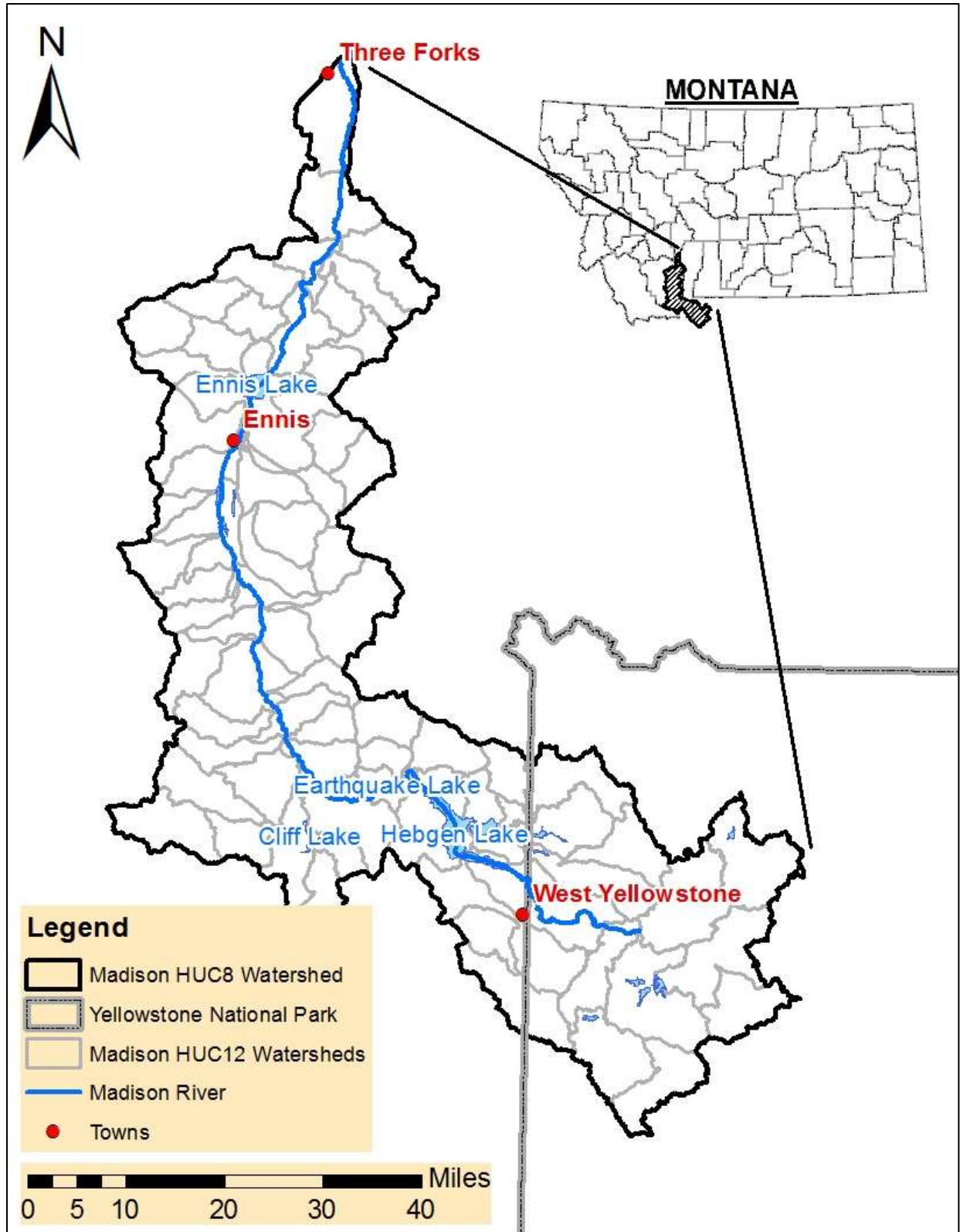


Figure 2-1. Location of Project Sub-basins

2.2 DATA COMPILATION

The necessary data for the DON included both nonanthropogenic and anthropogenic arsenic loads calculated from concentrations and flow volumes.

Existing data for the Madison Basin were compiled using the methodology described in the project QAPP (DEQ, 2015a). The results of this task were used to develop additional sampling efforts as described in the project SAPs (DEQ, 2015b, 2016b). The sampling objectives, sampling design, and data quality objectives are described in the project QAPP (DEQ, 2015a). Total recoverable arsenic concentrations, dissolved arsenic concentrations, total suspended solids, and flow volume for the mainstem of the Madison River along with tributary data were compiled into an Excel spreadsheet. Historical data locations and additional sampling locations are shown on **Figure 2-2**. The arsenic concentrations and flow data for the Madison River and associated tributaries are maintained at DEQ and are available upon request (DEQ, 2016c).

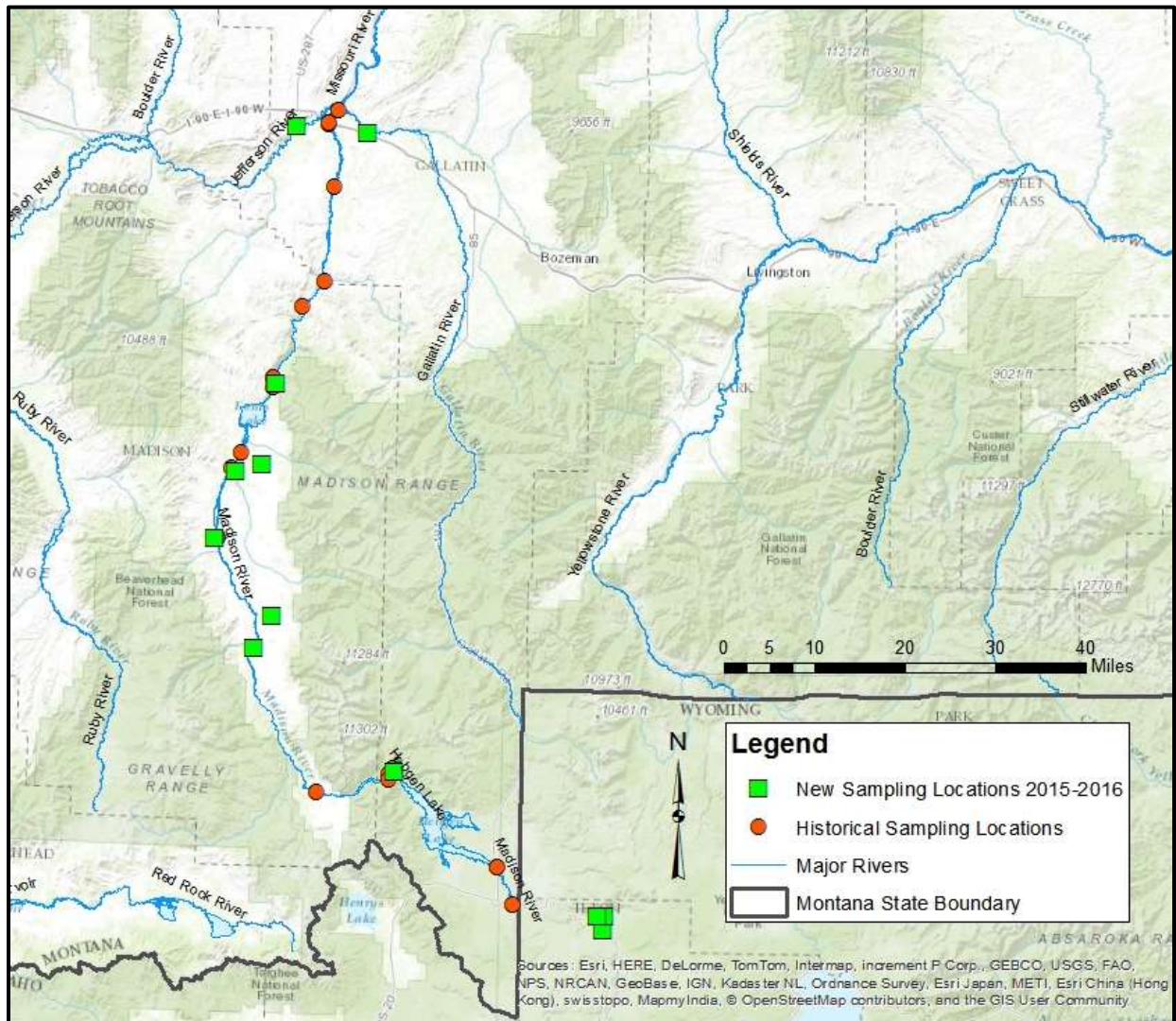


Figure 2-2. Map Showing Historic and Additional Sampling Locations

Due diligence was used to assess and collect data to determine the sources of arsenic to the Madison River. The following is a list of potential sources of both anthropogenic and nonanthropogenic arsenic and will be discussed in more detail in the following sections:

- Point Sources
- Overland Runoff
- Groundwater
- Tributaries

A publication that summarizes the different anthropogenic sources of arsenic in Montana can be found at: <http://toxsci.oxfordjournals.org/content/123/2/305.long>.

2.2.1 Point Sources

2.2.1.1 Permitted Point Sources

Permitted dischargers included major facilities legally and actively discharging into the project waterbodies. The arsenic concentration data was extracted from the EPA's Integrated Compliance Information System (ICIS) database. Only Montana facilities with effective or administratively extended permits in the project sub-basins were analyzed and discussed in **Section 4.0**.

Additional research was performed to determine if there were any other discharges from other point sources. Other potential sources included active or inactive mining operations, remediation sites, leaking underground storage tank sites, or hazardous waste sites. These sites are described in more detail in the following sections.

2.2.1.2 Abandoned Mines

DEQ maintains information on abandoned mines throughout Montana in a Geographical Information System (GIS) inventory from the Abandoned Mines program. While the database identifies the location of inactive mining projects, there was limited soil and/or water quality data. Typically only the high priority abandoned mines had soil or water quality data. The scanned hard copies of the sampling results for high priority mines with additional information about each site were searched on the DEQ website at <http://deq.mt.gov/Land/AbandonedMines/priority>. Internal DEQ and public GIS information was also searched at: <http://svc.mt.gov/deq/wmadst> and <https://deqgis.mt.gov/arcgis/rest/services>.

Additional information regarding water quality from abandoned mines was available from the Montana Bureau of Mines and Geology (MBMG) Groundwater Information Center (GWIC) database at <http://mbmggwic.mtech.edu>. The GWIC database contained primarily water well information but also included springs and mines and other miscellaneous sources. The database was searched using numerous categories including drainage basin and counties. The data included a field for site type with categories such as "mine", "mine drainage", or "tailings pond" used to assess mines as sources of contaminants.

The results of the DEQ GIS inventory, internal records, and GWIC searches are summarized in Section 4.2.2.

2.2.1.3 Remediation Response Sites

The DEQ GIS inventory of contaminant releases for the remediation response sites throughout Montana was searched. There were no water quality or soil data associated with the inventory but the database

did include the location, site name, DEQ contact name if available, and the period of operation for some sites. Specific information including water quality for these sites was available via the listed DEQ contact or the DEQ website at one of the following links:

- <http://deg.mt.gov/Land/FedSuperfund>
- <http://deg.mt.gov/Land/statesuperfund>
- <http://deg.mt.gov/Land/brownfields>

Internal DEQ and public GIS information was searched at: <http://svc.mt.gov/deg/wmadst> and <https://deggis.mt.gov/arcgis/rest/services>, respectively. The DEQ remediation division was also contacted and there were no additional remediation sites that could not be accessed from the aforementioned links.

2.2.1.4 Underground Storage Tanks (USTs)

An inventory of known leaking underground storage tank (LUST) sites is located at <http://deg.mt.gov/Land/lust/lustsites>. Many of the LUST sites had received financial reimbursement for cleanup efforts from the Montana Petroleum Tank Release Compensation Board (PTRCB). The water quality data of older sites was not available as an electronic spreadsheet or hardcopy. Internal DEQ and public GIS information was also searched at: <http://svc.mt.gov/deg/wmadst> and <https://deggis.mt.gov/arcgis/rest/services>, respectively. Additionally, the DEQ Petroleum Tank Cleanup Section was contacted and no additional LUST information was obtained.

2.2.1.5 Hazardous Waste

DEQ maintains a GIS inventory of hazardous waste handlers including the site name and the locations. These sites were not necessarily associated with contaminant releases unless they were also indicated as a remediation response site (see **Section 2.2.1.3**). Additional research was necessary if the information indicated that these sites were a source of contamination. Internal DEQ and public GIS information were searched and available at: <http://svc.mt.gov/deg/wmadst> and <https://deggis.mt.gov/arcgis/rest/services>, respectively. There were no hazardous waste sites identified.

2.2.2 Overland Runoff

The arsenic load attributed to overland runoff included both anthropogenic and nonanthropogenic sources. The nonanthropogenic sources were from the naturally occurring arsenic in the native soils and stream bank sediment. The anthropogenic inputs were from agricultural practices and any exposed surface conditions that resulted from industry, forestry practices, and/or fire. Mining and other industries were discussed as a potential point source load; however, these industries were considered when evaluating non-point source loads to both runoff and groundwater. The databases for these specific industries were covered in previous sections. This section is focused on the naturally occurring arsenic composition in the native soils and agricultural practices in the Madison basin.

2.2.2.1 Soil/Stream Sediment

The arsenic composition of the native soil was used for estimating the load to surface water from runoff events. Soils were not typically sampled for chemical characterization unless there was a release of contaminants into soil. The databases previously described for abandoned mines, specific remediation response sites and leaking underground storage tank sites had soil quality data for some of the sites used for determining sources of arsenic load to surface waters. Additional soil information for Montana, not associated with a potential release of contaminants, is available via a USGS report - Geochemical

and Mineralogical Maps for Soils of the Conterminous United States, USGS Open File Report 2014-1082 (Smith et al., 2014). This report summarizes the results of randomly distributed soil sampling across the United States, including 238 sites in Montana. The soil samples were collected at several depths and analyzed for numerous parameters. The report and data are available at: <https://pubs.usgs.gov/of/2014/1082>. DEQ maintains a GIS layer of all the sampling locations in Montana.

An additional USGS sediment data source, a national geochemical survey, is USGS Open-File Report 2004-1001 (USGS, 2008) available at: <https://mrdata.usgs.gov/geochem>. The USGS, in collaboration with other federal and state government agencies, industry, and academia conducted the National Geochemical Survey (NGS) to produce a body of geochemical data for the United States based primarily on stream sediments. The goal of the NGS was to analyze at least one stream-sediment sample in every 289 km² area by a single set of analytical methods across the entire nation.

Stream sediment quality for Montana streams are available via the abandoned mines databases described in the previous sections. Additional stream sediment information was available via the USGS National Geochemical Survey database at: <https://mrdata.usgs.gov/geochem>. This data portal includes GIS layers with quality data associated with each sample.

2.2.2.2 Agriculture

Agricultural practices in the Madison Basin may result in an increased anthropogenic load of arsenic to the Madison River. As irrigation water percolates through soil it has the potential to cause migration of contaminants that may be present in the soils and/or fertilizers/herbicides into local surface waters. Also, irrigation water may be diverted from one surface water source to another, thereby potentially migrating contaminants across watershed boundaries.

The Montana State Extension Service was contacted for purposes of determining whether arsenic was a common component in locally applied herbicides and pesticides. Dr. Cecil Tharp, a Pesticide Education Specialist at Montana State University, confirmed that lead arsenate pesticides had been effectively eliminated from use within the past 50 years. However, due to its persistence, it was possible that some soils still carry residuals. The use of arsenate pesticides was most common in late 19th and early 20th century orchards. Orchards are not common in the Madison basin or in Montana. Therefore, the anthropogenic risk of arsenic loading from arsenate pesticides is unlikely for the Madison Basin.

The DNRC water rights database for Montana was searched for agricultural points of diversion, points of use, and types of use. The types of uses included domestic, industrial, stock watering, agricultural irrigation, and lawn and garden. For purposes of determining anthropogenic effects, typically the use of concern was irrigation as that water was diverted, distributed on the land and a certain portion was eventually returned to surface water. Groundwater rights were also included in the database, and in some cases those contributed to migrating contaminants of concern from one basin to another. The result of research completed to assess the potential for agricultural inputs of arsenic to the Madison River is summarized in **Section 4.3.1**.

2.2.2.3 Modeling Runoff

Runoff water volumes were estimated based on topography, land cover, land use, soil-based runoff curves, and climate records. A standard method of calculating direct runoff from precipitation was developed by the Natural Resource Conservation Service (NRCS) using three variables: precipitation

totals, antecedent moisture conditions, and hydrologic soil-cover complex. Runoff was calculated as a percentage of the total precipitation computed from generalized parameters for soil, land cover, land use, and slope conditions.

EPA's Spreadsheet Tool for Estimating Pollutant Loads (STEPL) was the model used to determine the anthropogenic loading of arsenic from runoff events in the Madison basin. STEPL calculates loading of sediment, nitrogen and phosphorus based on land uses and spatially averaged soil attributes (Tetra Tech, 2011). STEPL uses the Universal Soil Loss Equation (USLE) to calculate sediment loads. The sediment load from each of the 64 Madison Basin HUC12s were individually calculated and first modeled under anthropogenic (existing) conditions.

Next, to determine the corresponding sediment loads under pre-anthropogenic (natural) conditions the existing conditions spreadsheet was modified. The modifications included setting all urban, cropland, and feedlot modeled acreage to zero and transferring that modeled acreage to pastureland use. Pastureland has the same characteristics in the USLE as typical rangeland. As the large majority of urban, cropland and feedlot development occurred in rangeland and outside the forests, this was a valid approximation of pre-anthropogenic conditions. The sediment load differences between the existing and natural condition spreadsheets were attributed to anthropogenic modified land uses. Examples of the STEPL spreadsheets are located in Appendix A.

STEPL input values were based on the county chosen (Gallatin and Madison for HUC8) and the most geographically comparable weather station (Missoula). The default STEPL values were used for this analysis with one exception, the distribution of urban land use was changed to match DEQ's Spatial Database Engine's SDE's Madison HUC8 urban land use percentages from the 2013 National Land Cover Database (NLCD). The advantage of using STEPL for a relative difference calculation (as above) was that much of the error associated with unknown starting conditions, parameters, etc. was largely muted when calculating relative values. Although this was not always the case, the relative error associated with using relative differences from STEPL calculations was typically much lower than that associated with using absolute values from STEPL.

The concentration of arsenic attached to the anthropogenically derived sediment load was based on extrapolation of the soil data from the USGS nationwide study on soils (Smith et al., 2014) as described in **Section 2.2.2.1**. The USGS soil data from the top 5 cm of soil was used in the analysis as that was the soil most likely to be transported with runoff. A summary of this data and associated land uses for the Missouri Basin is presented in **Figure 2-3**. The arsenic concentration of the only anthropogenic land use (planted/cultivated) was slightly less than the two land uses that approximate rangeland (herbaceous upland and shrubland). This was evidence that anthropogenic effects have little chance of affecting instream arsenic in the Madison watershed.

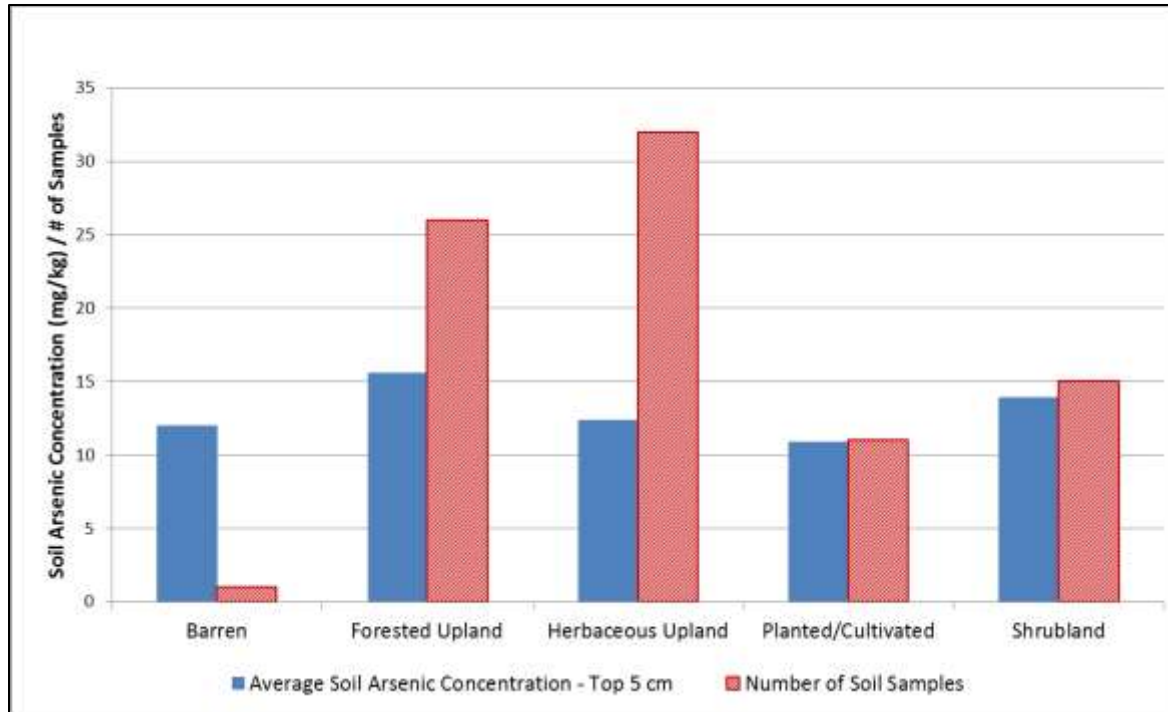


Figure 2-3. Soil Arsenic Concentrations in Upper Missouri Basin (adapted from Smith et al., 2014)

2.2.3 Groundwater

Concentrations of naturally occurring arsenic in groundwater varied regionally primarily due to geologic conditions. Unless proven otherwise, arsenic in groundwater was assumed to be naturally occurring and originating from the local geologic formations. In addition, the hyporheic zone can allow surface waters with naturally elevated arsenic concentrations to mix into the groundwater which can cause the groundwater to have similarly elevated arsenic concentrations. The arsenic mass loading to surface water from the groundwater was estimated from average groundwater arsenic concentrations.

Groundwater quality information was available through two databases: the GWIC database; and the USGS National Water Information System (NWIS). Both of these databases pulled information from outside entities (including but not limited to DEQ, EPA, BLM, USFS, county agencies, and private watershed groups) providing a large majority of existing groundwater data, but not necessarily all the existing data. These databases had overlapping data but are not identical; therefore, data from these two databases were combined and edited to remove duplicate samples. Other groundwater data was available separately from databases previously described for specific remediation response sites. The MBMG GWIC database is available at: <http://mbmggwic.mtech.edu>. The USGS NWIS database is available at: https://www.waterqualitydata.us/portal_userguide.

A state-wide groundwater arsenic map and corresponding GIS database was created by DEQ WQPB for the purpose of identifying locations with high arsenic groundwater concentrations (DEQ, 2016d). This database was searched to identify any anthropogenic and/or nonanthropogenic groundwater influences to the total arsenic load in the Madison River. The database was not published; however, it is available from DEQ's WQPB upon request.

2.2.4 Tributaries

The major tributaries were assessed for arsenic loading. This assessment included existing data or data collected during the monitoring portion of the project. The arsenic mass loading contribution was likely natural unless anthropogenic sources were identified, or values were unusually high or different than nearby reference streams. If an anthropogenic influence was identified, a percentage of the loading due to anthropogenic input was determined. The process of determining the anthropogenic sources in each of the tributaries was the same as discussed in the previous sections for the mainstems.

2.3 MASS LOAD ANALYSIS

2.3.1 LOADEST Modeling

Mass load is also referred to as mass flux when there is a continuous record of concentration and discharge (Aulenbach et al., 2007). Mass flux (Φ) is the product of constituent concentration (C) and discharge (Q) integrated over time (t).

Equation 1:

$$\Phi = \int C(t)Q(t)dt$$

The approach used to estimate concentrations continuously through time was a regression-model method for estimating fluxes (Aulenbach et al., 2007). The regression-model method, also known as the rating-curve method, is a standard statistical technique that is used to estimate concentration continuously, thus enabling a direct calculation of mass flux (Aulenbach et al., 2007). This method uses a regression model relating concentration to continuous variables such as discharge or time.

A computer program used for estimating arsenic load is the USGS program LOADEST (Load Estimator). Given a time series of streamflow, additional data variables, and arsenic concentrations, LOADEST produces regression models for the estimation of arsenic (Runkel et al., 2004). Explanatory variables within the regression model include various functions of streamflow, decimal time, and additional user-specified data variables. The formulated regression model is then used to estimate loads over a user-specified time interval. Mean load estimates, standard errors, and 95 percent confidence intervals are developed on a monthly and/or seasonal basis. The calibration and estimation procedures within LOADEST are based on statistical estimation methods. LOADEST output includes diagnostic tests and warnings to assist in determining the appropriate estimation method and in interpreting the estimated loads (Runkel et al., 2004). Essentially the program finds a best fit data model of flux as a function of discharge, then extrapolates these relationships to estimate flux from daily flow data. The two input files were flow data and water quality data. For this project, daily flow data were obtained from existing USGS gaging stations, and water quality data (total recoverable arsenic concentrations) were obtained from periodic grab samples taken by either USGS or DEQ. These samples were typically collected on a monthly basis and included an associated flow value. The model required a minimum of twelve concentration data points. The model outputs included annual and monthly load averages (kg/day) and concentration averages ($\mu\text{g/L}$), daily load (kg/day) and concentration ($\mu\text{g/L}$) estimates, and calibration and modeling statistics. The outputs presented in this document incorporated a Maximum Likelihood Estimation (MLE) technique for the daily and monthly loads.

2.3.2 Synoptic Mass Load Analysis

When there was less concentration data and/or the river or stream location was not a USGS gaging station, the alternative synoptic mass load analysis was used to calculate a mass load. This approach was

also used for point source discharges. The mass load analysis was defined by a direct calculation of mass load using the following equation:

EQUATION 2: $ML = C \times Q \times t \times cf$

Where,

ML – Mass Load (pounds or kilograms)

C – Concentration (µg/L or mg/L)

Q – Flowrate at a point (cubic feet per second, cfs)

t – A period of time (season, month, or year)

cf – conversion factor for mass load calculation (variable depending on units of individual terms)

For each sample pair collected (flow and concentration), a mass load was calculated. A median or average of the calculated mass load was used in the mass balance equation (**Section 2.4**).

This process is simpler than the process described in **Section 2.3.1**. The advantage of using synoptic mass load analysis is that a load is estimated with less data and without a USGS gaging station. The disadvantage is that the results are only as reliable as the data collected. For instance, if the data is highly variable with limited seasonal representation, the mass load results have the same limitations. For all mass load calculations, incorporating more data with seasonality and annual fluctuations is best for statistically valid results. Data needs and statistical validity for mass load analysis are discussed further in **Section 3**.

2.4 MASS BALANCE APPROACH

The mass balance approach offers a useful technique for quantifying the transport of trace elements such as arsenic in surface water. In mass balance considerations, data on both hydrological conditions and the chemical quality of water are taken into account simultaneously. A mass load is the mass of arsenic transported at a point in a waterbody during a period of time.

A simple mass balance model was used for the Madison River arsenic load. The equation is as follows:

EQUATION 3: $TAL = YNP + PSL + GW + Trib + RO$

Where,

TAL – Total arsenic load

YNP - Geothermal arsenic load from the Yellowstone Caldera

PSL – Point source arsenic load, permitted discharge operations

GW – Groundwater arsenic load contribution

Trib – Arsenic load associated with surface water discharge into the mainstems from the major tributaries

RO – Non-point source runoff arsenic load

The individual terms in **Equation 3** describe a mass load. Each mass load is defined by the mass load equation (**Equation 2**). **TAL** is the total arsenic load in the stream which includes both “nonanthropogenic” and “anthropogenic” sources. Therefore, **TAL** was rewritten to express this relationship.

EQUATION 4: **TAL = NAL + AAL**

Where,

NAL = Nonanthropogenic Arsenic Load

AAL = Anthropogenic Arsenic Load

It is important to understand the relative contribution of nonanthropogenic arsenic load versus that known to occur from anthropogenic sources. To distinguish between nonanthropogenic and anthropogenic sources of arsenic, the mass balance equation (**Equation 3**) is written as:

EQUATION 5: **TAL = YNP + PSL + GWA + GWN + TribA + TribN + ROA + RON**

Where,

GWA – Groundwater mass load contributions considered anthropogenic

GWN – Groundwater mass load contributions considered nonanthropogenic

TribA – Tributary mass load contributions considered anthropogenic

TribN – Tributary mass load contributions considered nonanthropogenic

ROA – Surface water runoff with anthropogenic derived arsenic loading

RON – Surface water runoff with nonanthropogenic derived arsenic loading

Equations 3, 4, and 5 is rearranged to solve for **NAL** and expressed as:

EQUATION 6: **NAL = TAL - PSL - GWA - TribA - ROA**

3.0 DATA NEEDS

A thorough search of all available databases, as described in **Section 2.0**, was likely to produce enough information to determine whether there were anthropogenic influences in the watershed. However, if there was a question regarding anthropogenic influence, missing data in tributaries, or other concerns about data limitations, additional sampling was required. In the Madison River, there was adequate sampling on the main-stem and the major tributaries, but after reviewing the minor tributaries, it became clear that several tributaries with either some mining history or high arsenic soil concentrations had no data available, and several others had old data where detection limits were very high. Therefore, additional sampling was performed on several tributaries to fill in these data gaps.

3.1 DETERMINATION OF SUFFICIENT DATA

Figure 3-1 is a decision flowchart showing the process of determining whether additional sampling was needed.

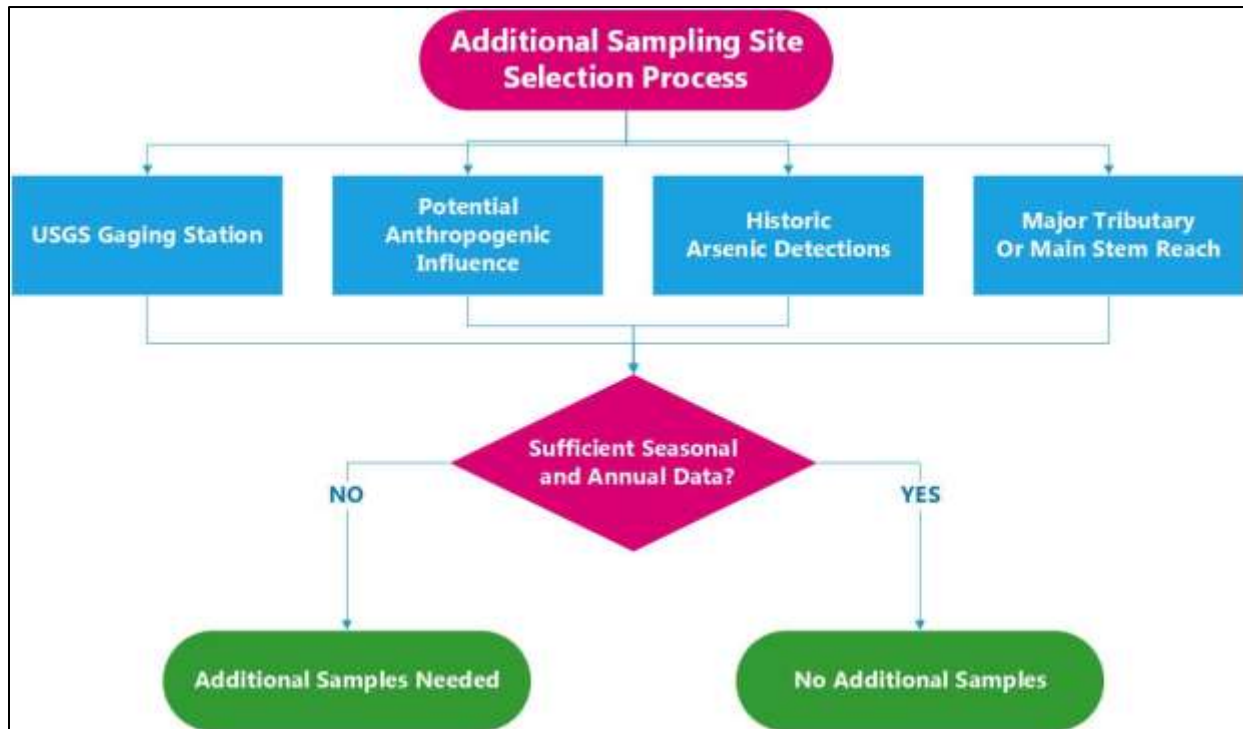


Figure 3-1 Decision Flow Chart for Additional Sampling for Tributaries

After completing all database searches and compiling the anthropogenic and nonanthropogenic data into one dataset, an analysis was performed as to whether sufficient data existed to complete a defensible and valid DON. The process of determining whether there was sufficient data is presented in **Figure 3-2**.

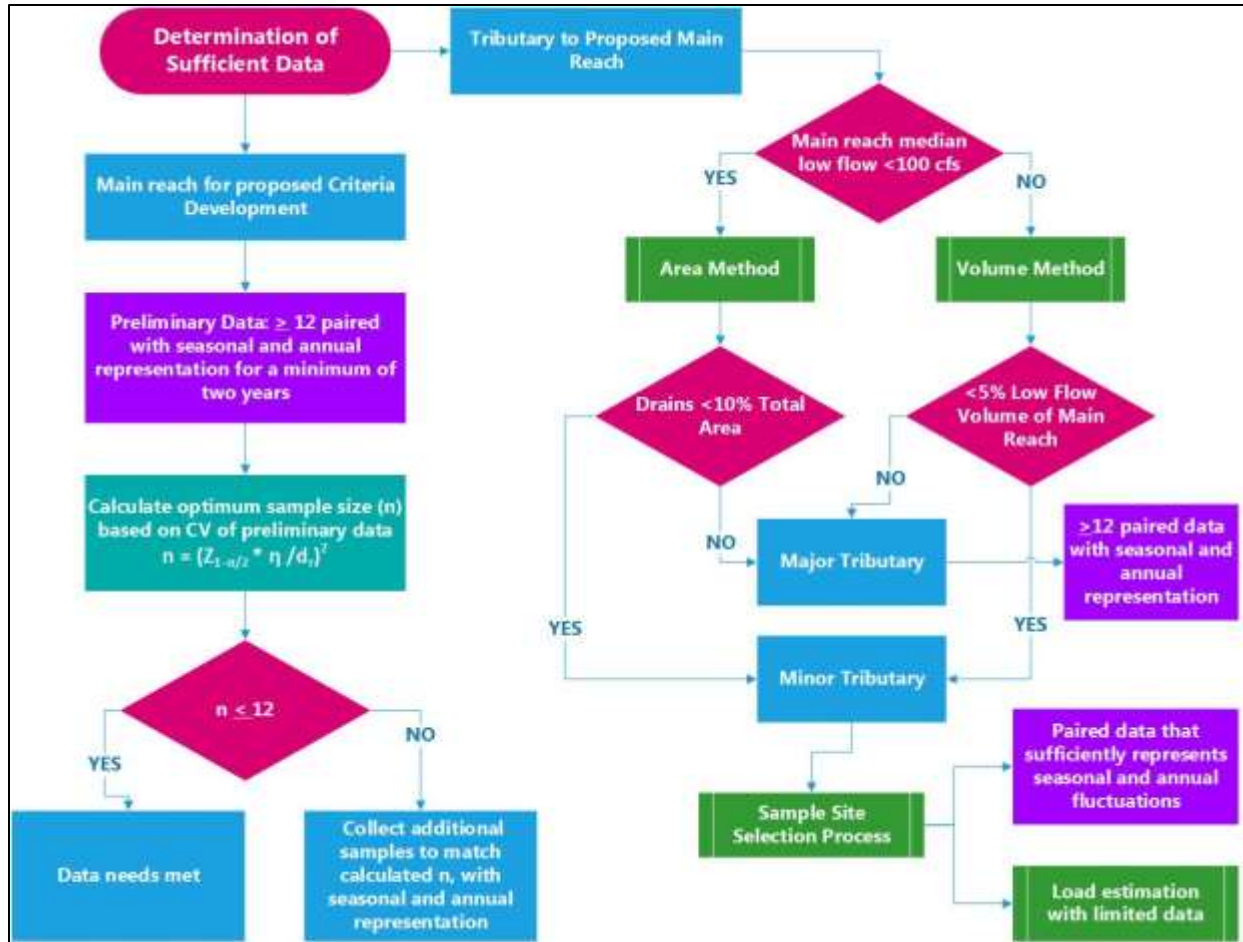


Figure 3-2. Flow Chart for Determination of Sufficient Data

For the major tributaries and main reaches in the Madison River watershed, 12 paired water quality and flow samples with seasonal and annual representation for a minimum of two years was collected. The following sections explain how these numbers were determined.

3.2 SAMPLE SIZE DETERMINATION

Most methods for sample size determination required some knowledge about the desired outcome and population in advance, including:

- Desired accuracy of results
- Confidence level; and
- Variability of data

While the desired accuracy and confidence can be determined *a priori*, understanding the variability of the data required some knowledge of the population. Metrics such as standard deviation (σ), mean (μ), and the coefficient of variation (CV) or relative standard deviation (σ/μ), have a huge influence on the spread of the data and thus confidence intervals, prediction intervals, etc. The central tendency of datasets with high variability can be very difficult to characterize by sampling. Consider which population in **Figure 3-3** would be easier to characterize with just a few samples. Stream A would be easier to characterize with fewer samples since there is less variability in the concentration data.

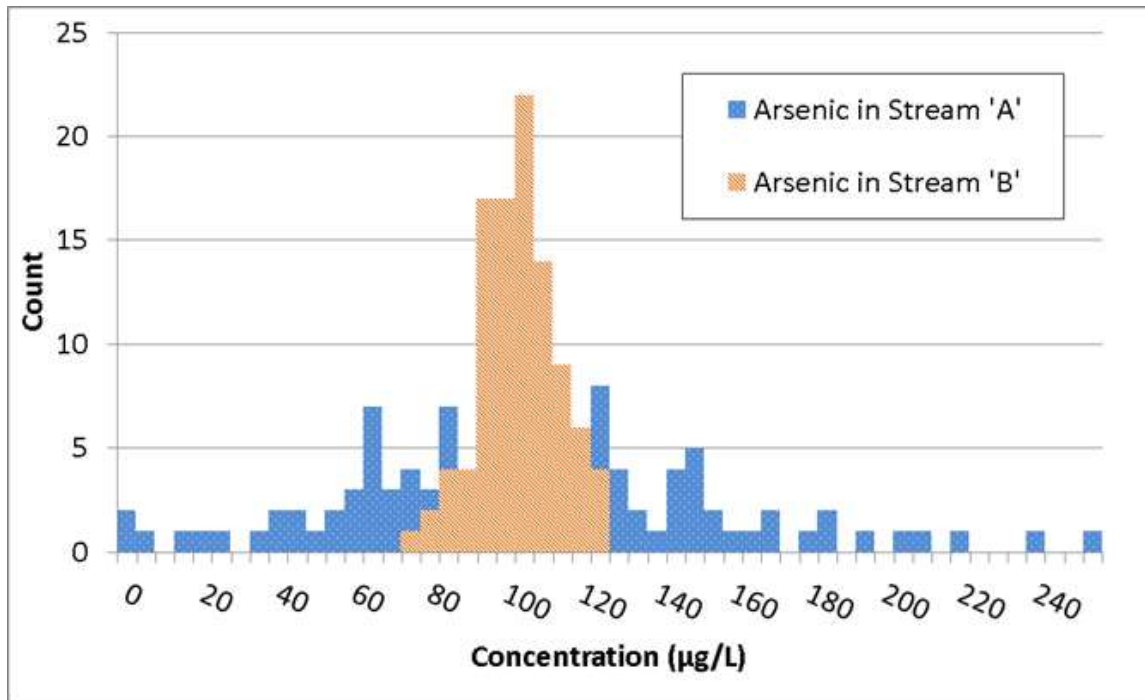


Figure 3-3. Examples of Variability Between Environmental Datasets

The CV is very useful as it allows comparison of any given sample dataset's standard deviation to all other sample datasets' standard deviations (DEQ, 2011), regardless of whether the arsenic concentrations in the datasets are high, low, or in between. The required sample size depends on the coefficient of variation (CV). Data sets with a low CV require a handful of samples to achieve a strong estimate of means, whereas datasets with a high CV require hundreds of samples.

One of the most common methods to determine sample size in environmental data is to implement a two-stage sampling procedure. In this process, preliminary data is collected from the population to approximate the relative standard deviation, and then the necessary sample size is calculated from this data (with a predetermined confidence level and acceptable error). Then, if the required sample size is less than what had already been collected, data collection is complete. If the required sample size is larger than what had already been collected, more data is needed. This method is common (Gilbert, 1987) and provides a good estimate of needed sample size. The formula for calculating sample size with a pre-determined relative error is:

EQUATION 7:
$$n = (Z_{1-\alpha/2} * \eta / d_r)^2$$

Where n is the required number of samples, Z is the standard normal deviate (often looked up in statistical tables) for the confidence level desired, α is the desired significance level, η is the coefficient of variation or relative standard deviation, and d_r is the pre-specified relative error from the mean. The advantage of this method is simplicity, but one disadvantage is that it may not account for asymmetry and non-normal distributions.

The size of the preliminary data set is somewhat arbitrary, but 12 samples are suggested. This sample size is more than 10, which several sources suggest is a minimum for capturing adequate seasonal and annual variability, and less than the 30 that is typically considered a large data set in statistics.

Additionally, the Madison River load data sets described in the next section, some of which have low CV values for environmental data, had optimal sample sizes that straddle 12 based on a 90% confidence level and 15% error. In other words, the collection of 12 samples allowed 90% confidence that the load calculated for a Madison River station was within $\pm 15\%$ of the *true* load. Data sets with lower CV than these sets would be unusual. Thus, to determine the required sample size, 12 preliminary samples were collected (making sure they are spatially and/or temporally independent as needed) to determine the approximate variance and mean. Then, using a pre-specified relative error and a confidence interval, the required sample size was determined. At this point, more samples may have been required.

Another methodology that was available is the bootstrap method. The bootstrap method (or bootstrapping) refers to any test or metric that relies on random sampling with replacement and assigns measures of accuracy such as a confidence interval or standard deviation based on this random sampling. The bootstrap method provided better estimates of medians and reduced the required sample size. The bootstrap method requires a large amount of data up front, and assumes that this data accurately represents the true population. But once those requirements are met, especially for the large Madison River datasets, it provides greater detail than traditional methods.

Bootstrapping is performed for a set number of samples (n) taken from a sub-set of the data. The bootstrap sample is taken from the census using sampling with replacement and repeated multiple times (1,000 or 10,000 times are common). For each of these bootstrap samples, a mean (or median) is computed. The result is a histogram of bootstrap averages that provides an estimate of the shape of the distribution of the mean (**Figure 3-4**).

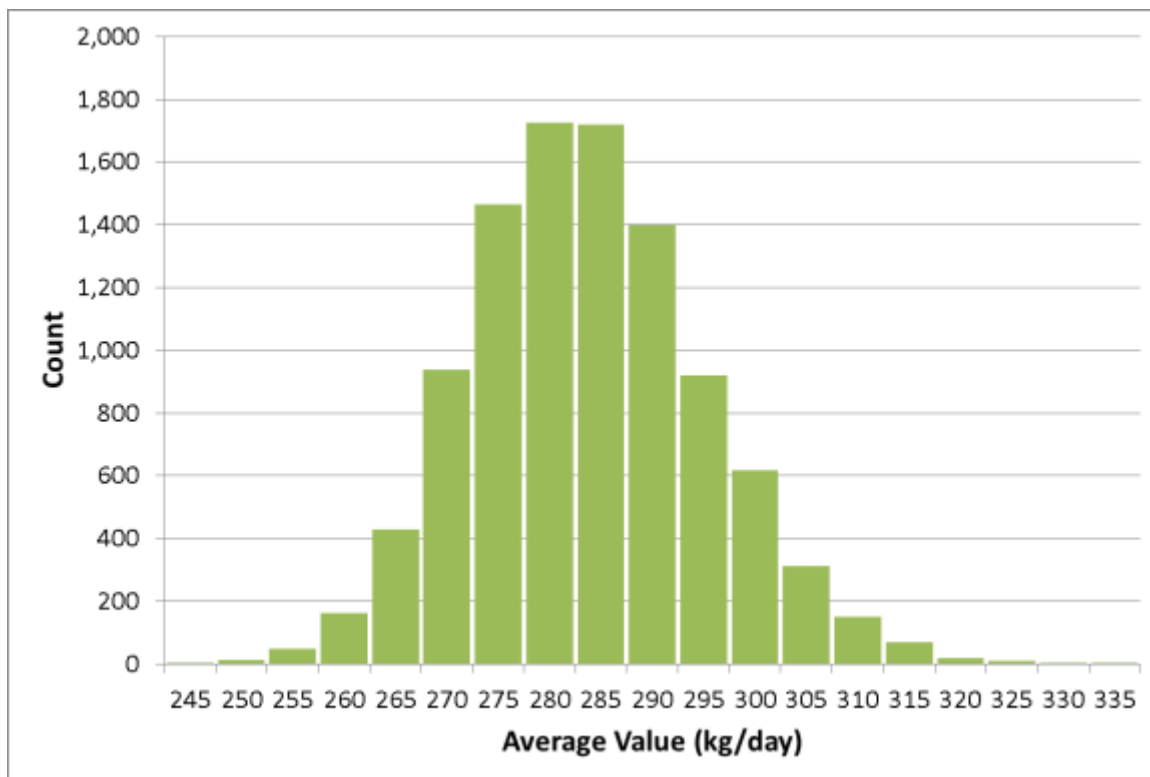


Figure 3-4. Example Histogram of Bootstrap Averages on Madison River Arsenic (10,000 replications)

From this, confidence intervals and other metrics are calculated. By varying the number of samples taken (n), distributions are compared and the optimal amount of data to collect is decided (**Figure 3-5**).

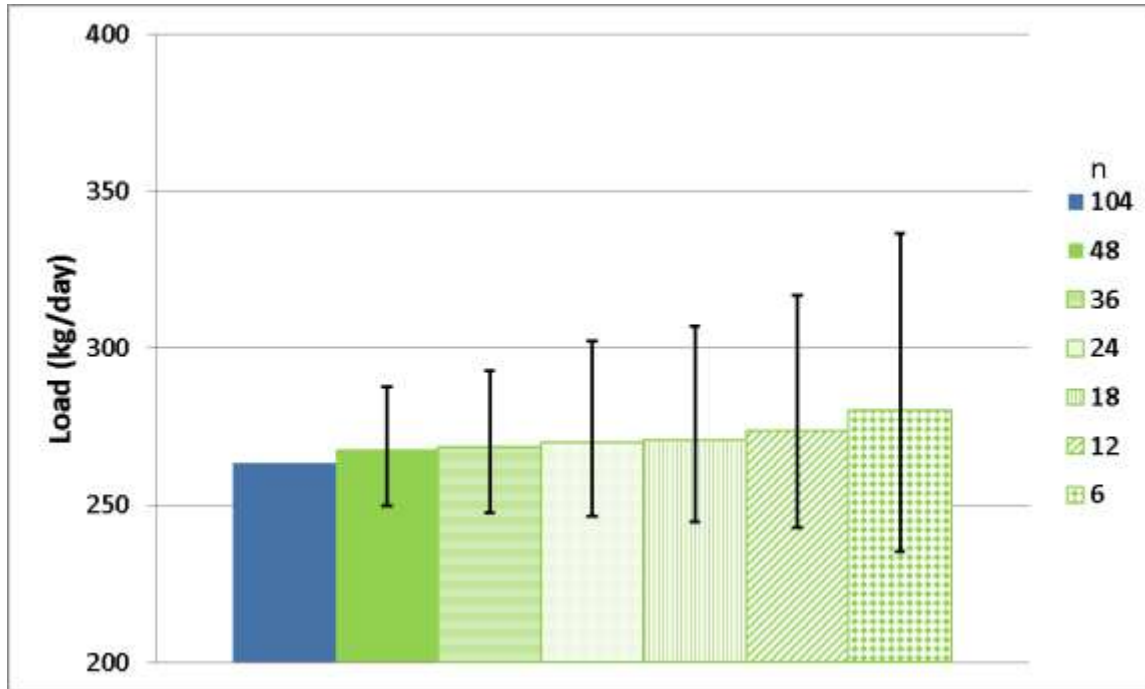


Figure 3-5. Bootstrap Results for Madison River below Ennis Lake Showing the Median Loads with Associated 90% Confidence Intervals for Each Sample Size

To determine the optimal number of samples for criteria development and to see how well it aligns with estimates from traditional simple random sampling methods, the Madison River at West Yellowstone data set was analyzed using both methods (simple random sampling and bootstrapping). This data set has 105 samples and the coefficient of variation (standard deviation/mean) is 0.275. Using a 90% confidence level and an acceptable 15% error in the results, an n of 9.1 was calculated using **Equation 7**. Therefore, to achieve a 15% error (or less), 10 (rounding 9.1 to the next whole number) is the minimum number of samples. When applying this method to the Madison River at Ennis dataset (104 samples, $CV = 0.451$), an n of 25 was calculated using **Equation 7**, meaning 25 is the minimum number of samples collected to achieve a 15% error (or less).

To follow up with a secondary check and to see if the simple method was reasonably estimating sample sizes, a bootstrap analysis was performed on the medians of the Madison River datasets and the 90% confidence level was calculated. The bootstrap method was run 10,000 times for each sample size. As mentioned, both Madison River datasets are robust, with greater than 100 samples per station. Since each data set is large and incorporates annual and seasonal fluctuations, the data set accurately represents the population and therefore meets the assumptions associated with bootstrapping. The original data set is called the census and is shown in blue on **Figure 3-5 and 3-6**. The bootstrap samples were chosen for n equal to 48, 36, 24, 18, 12, and 6 as shown in green on **Figure 3-5 and 3-6**. The 90 percent confidence interval is presented as an error bar for each sample size in **Figure 3-5 and 3-6**. The confidence interval is slightly skewed, with the upper confidence interval further from the median value, because the original data set is skewed and not normally distributed.

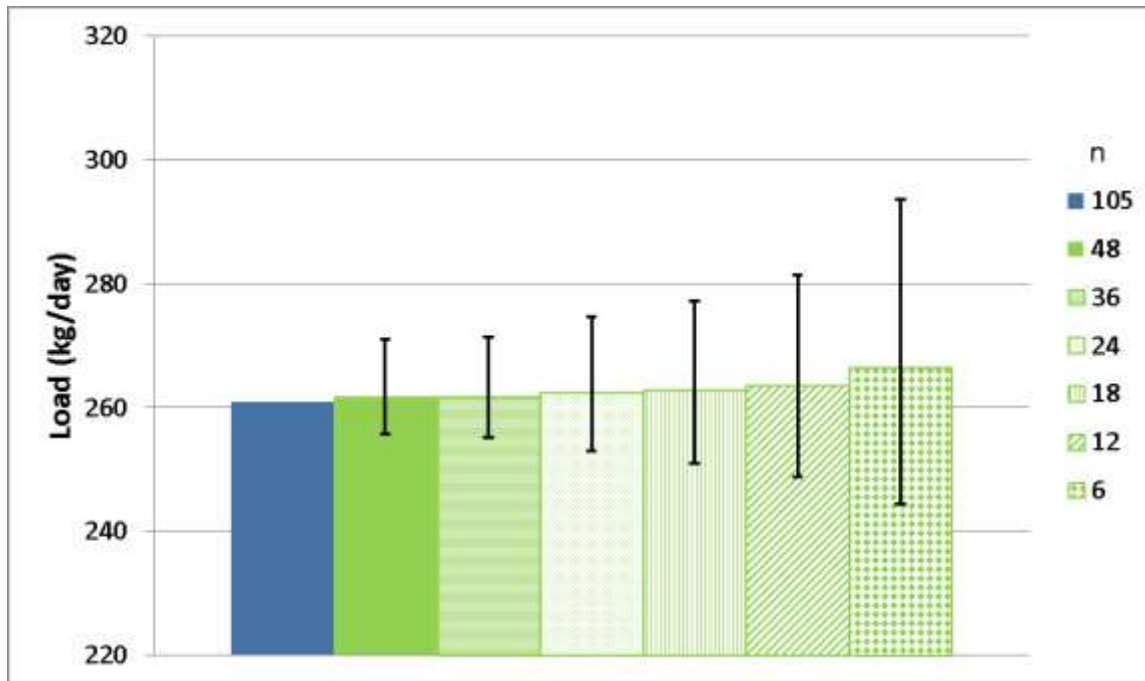


Figure 3-6. Bootstrap Results for Madison River at West Yellowstone Showing the Median Loads with Associated 90% Confidence Intervals for Each Sample Size

The 90% confidence interval for the varying sample sizes is presented as a percent in **Figure 3-7 and 3-8** for the two Missouri River stations. As the sample size decreases the range of the confidence intervals increase. A sample size of 48 has the narrowest confidence interval for both stations. This narrow range results from less variability within the original dataset – that is, the total load at these stations remains relatively constant over days, seasons, and years. For instance, for the Madison West Yellowstone station, sample sizes between 6 and 12 (actual number = 8) resulted in a 90% confidence interval of less than $\pm 15\%$ error (**Figure 3-7 and 3-8**). This slightly reduces the number of samples required in the initial simple sampling estimate of 10. In contrast, larger sample sizes between 24 and 36 (actual number = 30) for the Madison Below Ennis Lake station were needed to result in the same narrow range of approximately $\pm 15\%$. This number increases the number of samples required in the initial simple sampling estimate of 25, likely due to the skewness or naturally higher variability of the data.

Other Montana rivers and streams showing more seasonal and annual variability will likely have higher variability. These will require greater sample sizes for statistical reliability. The flow chart shown in **Figure 3-2** captures the increased data requirements for data sets that have larger CVs.

Therefore, the minimum dataset required for Madison River at West Yellowstone is 10 samples, and the minimum dataset required for the Madison River at Ennis is 25. These datasets include both flow and concentration. Fortunately, there is an abundance of flow and concentration data for the Madison River and major tributaries that more than meets the minimum criteria established in this section.

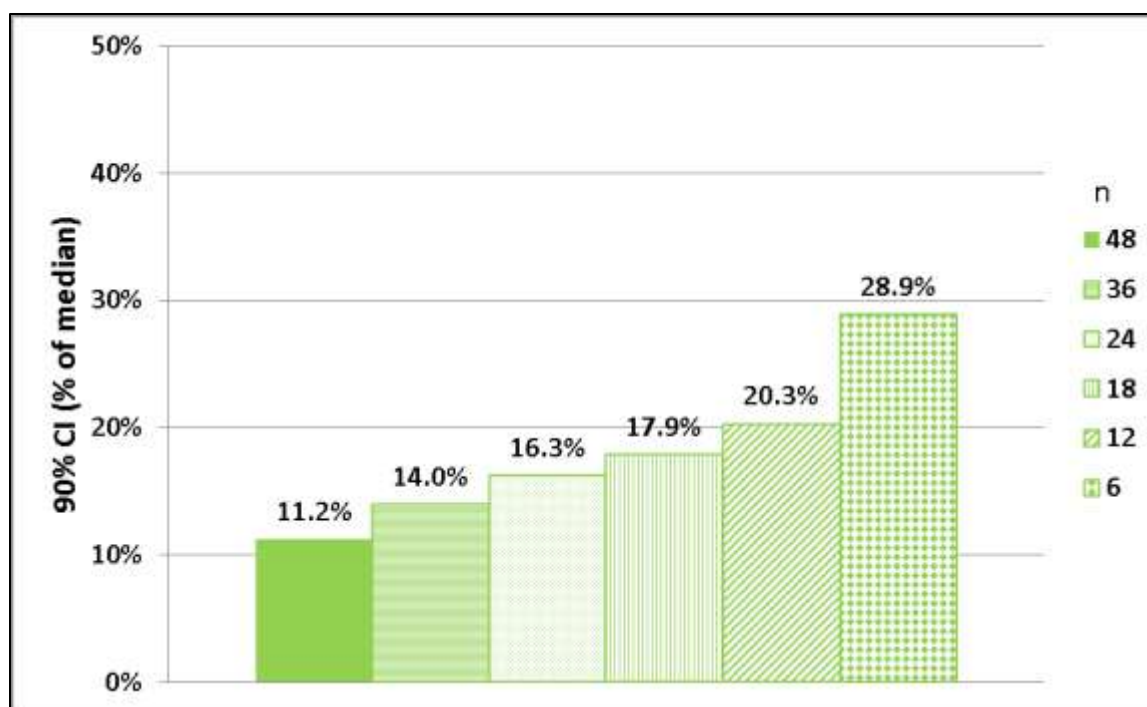


Figure 3-6. Bootstrap Results for Madison River below Ennis Lake Showing 90% Confidence Intervals for Each Sample Size

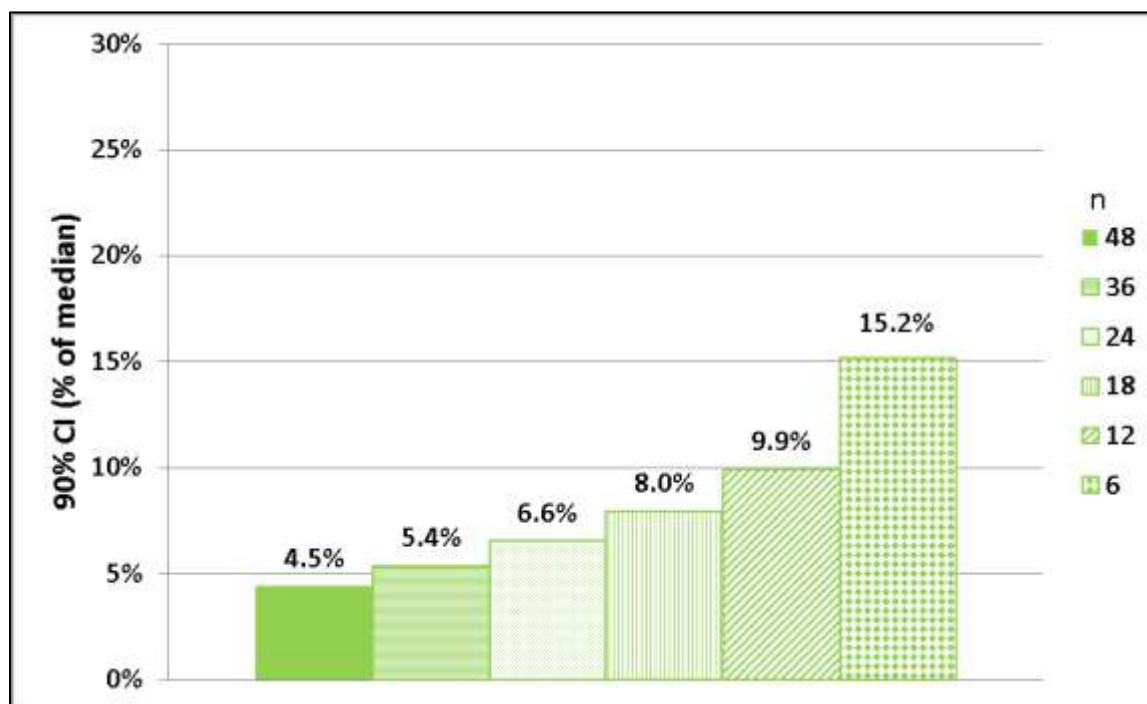


Figure 3-6. Bootstrap Results for Madison River at West Yellowstone Showing 90% Confidence Intervals for Each Sample Size

4.0 RESULTS

4.1 HYDROLOGIC SEGMENTS

The Madison River and associated tributaries were divided into three hydrologic sections for the mass balance analysis. The sections were based on the regional hydrologic divisions caused by the dam infrastructure, and are shown in **Figure 4-1**. The three hydrologic sections are:

- West Yellowstone to Hebgen Lake
- Below Hebgen Lake to Ennis Lake
- Below Ennis Lake to the mouth of the Madison River

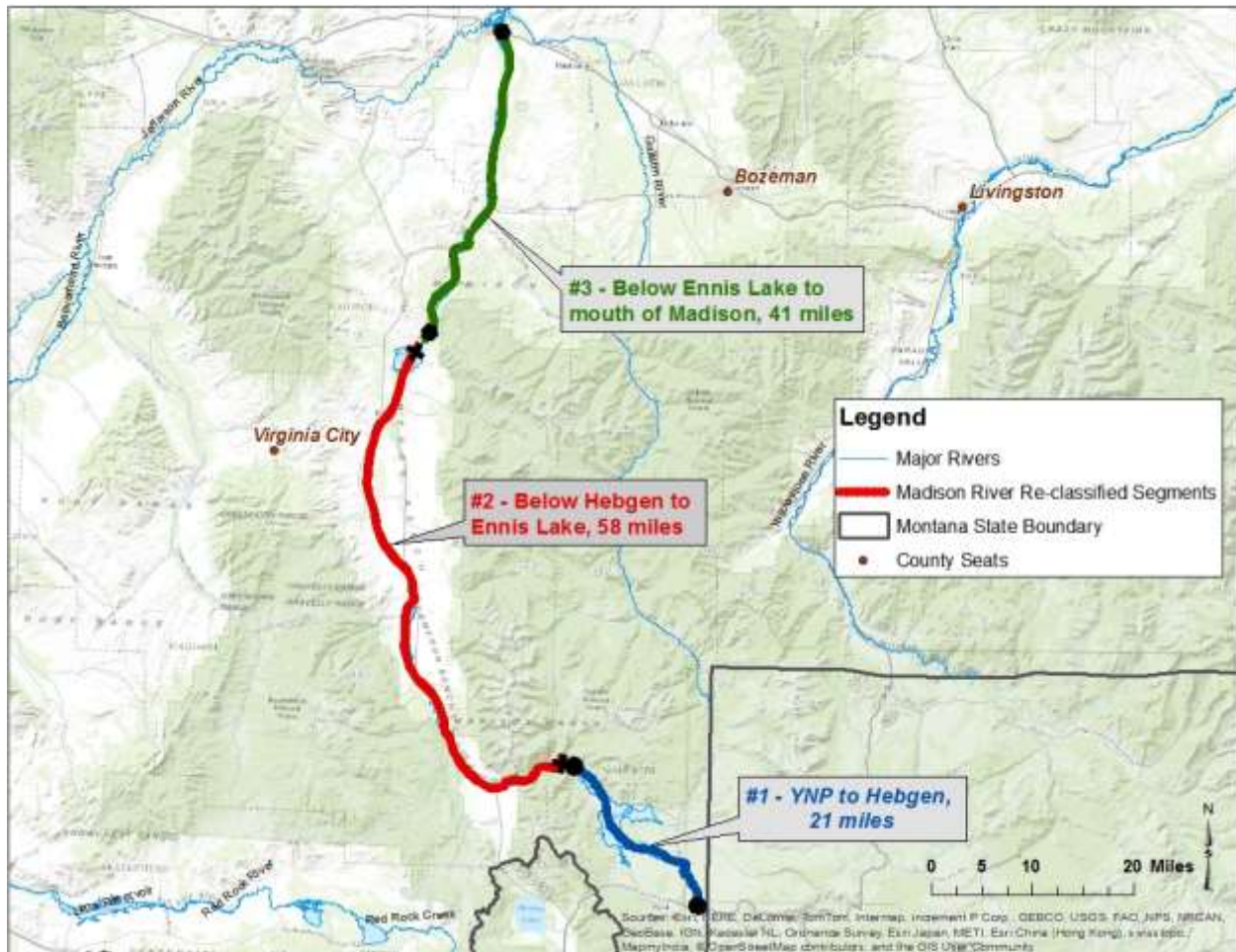


Figure 4-1. Hydrologic Sections of the Madison River for Mass Balance Analysis

The arsenic loads and concentrations become homogenized within the reservoirs as a result of the detention time within the reservoir. Each segment has a vastly different median concentration. As the river leaves YNP, arsenic concentrations are high from natural geothermal sources. Tributaries dilute these high arsenic concentrations resulting in successively lower concentrations downstream from YNP in the Madison River.

4.2 POINT SOURCES

4.2.1 Permitted Discharges

The list of permitted discharges, average facility arsenic load, and the median ambient river load is listed in **Table 4-1**. A high flow (June) and low flow (December) arsenic load and the associated percentage of the total arsenic load in the river is presented.

Table 4-1. Permitted Dischargers

| MPDES No. | Facility | Receiving Body | Facility Load (Kg/ Month) | River/ Creek Load at Facility (Kg/ Month) | % of River/ Creek Load | Facility Load (Kg/ Month) | River Creek/ Load at Facility (Kg/ Month) | % of River/ Creek Load |
|-----------|--------------------------------|---------------------|---------------------------|-------------------------------------------|------------------------|---------------------------|-------------------------------------------|------------------------|
| | | | June | | | December | | |
| MTG130008 | USFWS- ENNIS NAT FISH HATCHERY | BLAINE SPRING CREEK | 3 | 1,290 | 0.233% | 3 | 840 | 0.357% |
| MT0030732 | ENNIS WWTP | MADISON RIVER | 0.18 | 9,625 | 0.002% | 0.15 | 10,327 | 0.001% |
| MT0000264 | THREE FORKS DOMESTIC WWTF | MADISON RIVER | 1.26 | 12,464 | 0.010% | 0.45 | 8,563 | 0.005% |

The Ennis Fish Hatchery does not have an arsenic limit within their permit but is a potential source of anthropogenic arsenic to Blaine Spring Creek, a tributary of the Madison River above Ennis Lake. The facility arsenic load presented in the table is a percent of Blaine Spring Creek arsenic load and not the Madison River. The Fish Hatchery load is approximately 0.03% of the total arsenic load in the Madison River at the convergence of Blaine Spring Creek.

Ennis Hot Springs (Permit #MT0028843) historically discharged into Moore Creek, a tributary of the Madison River prior to Ennis Lake. The facility no longer has a valid permit and was not included as an arsenic point source for this mass balance analysis.

The anthropogenic arsenic loads from the permitted discharges accounted for a very small percent of the total arsenic load in the Madison River. Regardless, these small loads were accounted for in the mass balance.

4.2.2 Mining

USGS sediment concentrations for the Madison basin are shown in **Figure 4-2** (Smith et al., 2014). The highest concentrations occur in three drainages in the eastern half of the Madison Basin, Indian Creek, Upper Bear Creek and Burger Creek drainages.

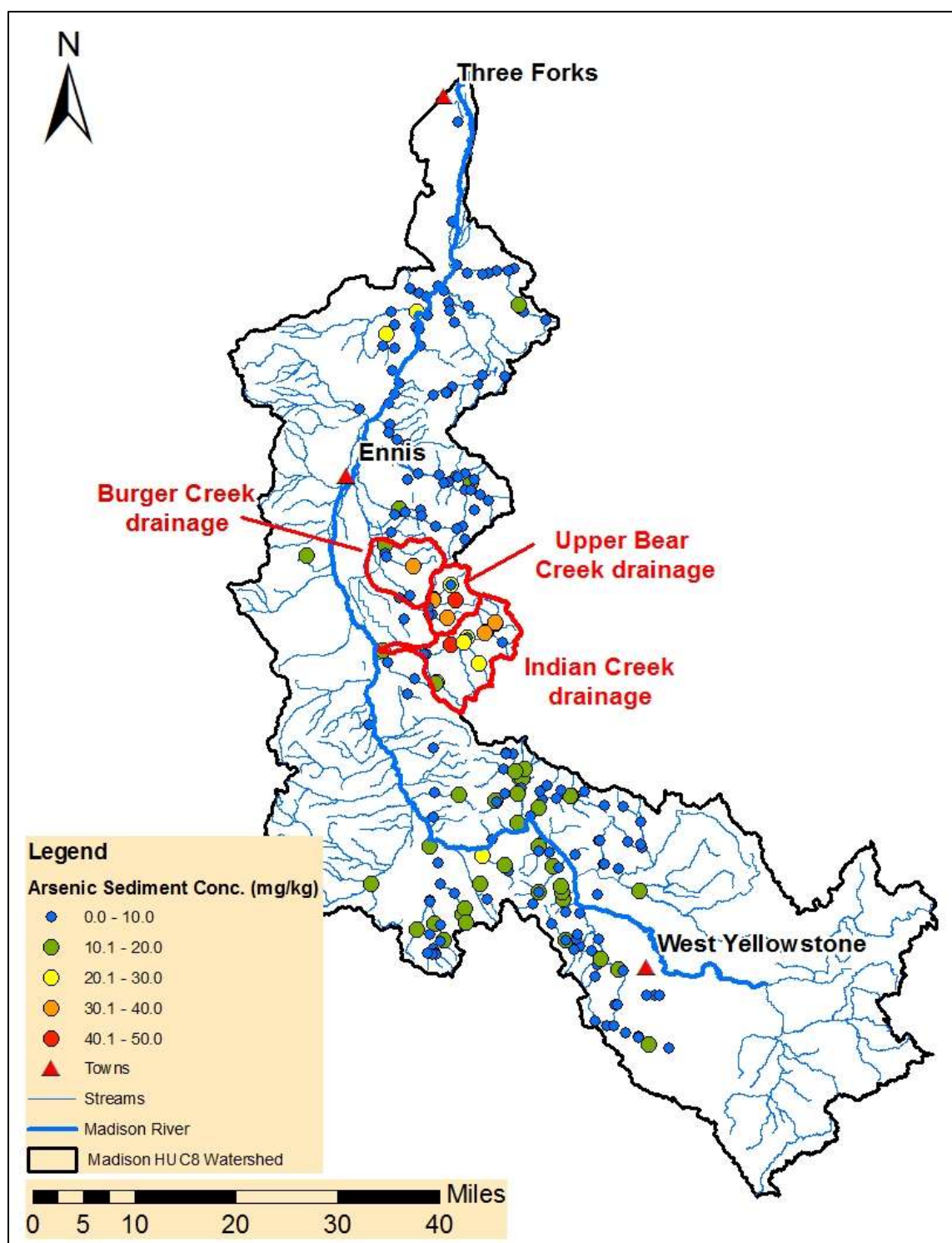


Figure 4-2. USGS Sediment Arsenic Concentrations for Madison Basin (Smith et al., 2014)

There were no mine remediation sites identified within these three drainages. The elevated concentrations are located on United States Forest Service (USFS) land. The Burger Creek drainage has the only known abandoned mine of the three drainages. There were no identified abandoned mines in the Indian or Upper Bear creek drainages but they both show similar if not higher arsenic sediment

concentrations than Burger Creek drainage. Therefore, the sediment arsenic concentrations in the Burger Creek drainage are more likely to be natural, similar to the neighboring Indian and Upper Bear Creek drainages.

This assumption of natural sediment concentrations is further evidenced by comparing the arsenic concentrations in the Madison to the entire Missouri Basin as shown in **Figure 4-3**. The Madison Basin sediment concentrations are similar to most of the other Missouri Basin sediment concentrations with the exception of higher concentrations in the Butte and Helena regions, which are likely due, in part, to mining impacts.

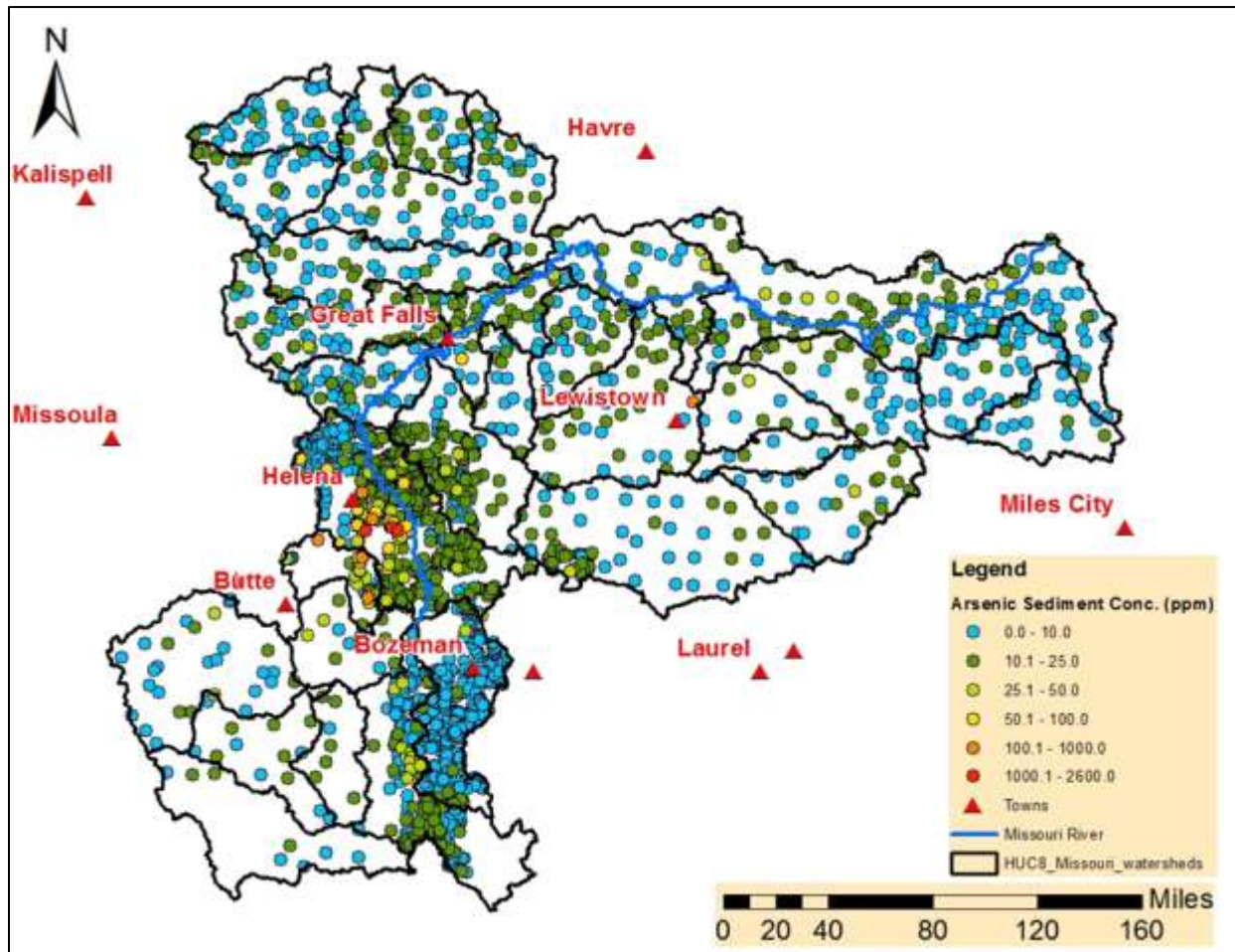


Figure 4-3. Upper Missouri Basin Stream Sediment Arsenic Concentrations (USGS, 2008)

A map showing data from the DEQ's Abandoned Mines program database and the MBMG GWIC database is shown in **Figure 4-4**. There are 115 inventoried abandoned mines in the Madison Basin with 110 concentrated near Ennis. Several of the abandoned mines are high priority cleanup sites with associated sediment, mine drainage and surface water data. The only elevated sediment concentration sample (290 mg/kg) was collected in South Meadow Creek (see **Figure 4-4**). The sample was taken below an abandoned mine tailings pile. A water sample taken in the same location in South Meadow Creek resulted in an arsenic concentration of 3.35 µg/L—well below the human health standard of 10 µg/L—indicating the elevated soil arsenic concentration was not contributing significant loading to surface water. The other elevated arsenic water sample (32.9 µg/L) was collected directly from an adit discharge

near South Meadow Creek - although the adit is not reported to flow into South Meadow Creek or the Madison River. Surface water and sediment sample results from abandoned mines near Hot Springs Creek and Elk Creek (**Figure 4-4**) had low arsenic concentrations. Based on this available data there is low potential for significant mining related sources of arsenic to enter the Madison River.

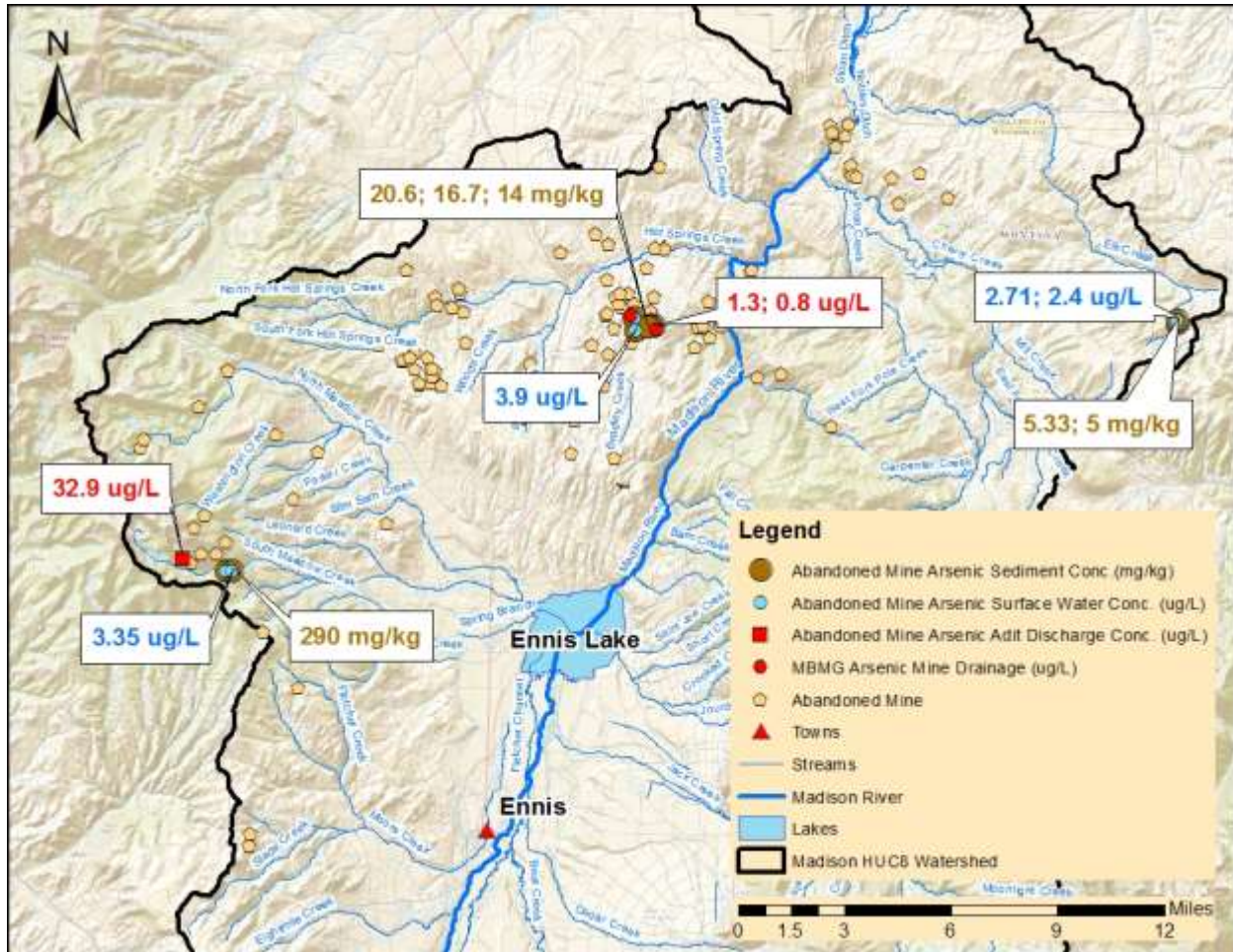


Figure 4-4. DEQ's Abandoned Mines Program Streambed Sediment, Adit Drainage and Surface Water Concentrations for Madison Basin. The red concentrations are adit/mine drainage, blue values are surface water concentrations, and brown values are sediment concentrations.

4.2.3 Other Anthropogenic Sources

Chromated copper arsenate is still in use as a wood preservative in industry. There did not appear to be evidence of industrial wood treatment facilities in the Madison basin. Other common commercial uses of chromated copper arsenate have been discontinued for over 50 years and residuals are not expected to be present in the Madison Basin. There were no hazardous waste sites identified during the records search for the Madison Basin.

Other potential anthropogenic point sources of contaminants to the Madison Basin are shown in **Figure 4-5**. These sources are based on the DEQ database for remediation response sites (RRS), but they are small sites and unlikely contributing any significant loads of arsenic into the basin. In addition, there are dozens of LUST sites that have had remediation work, but those sites are not sampled for arsenic as it is not a concern in petroleum products.

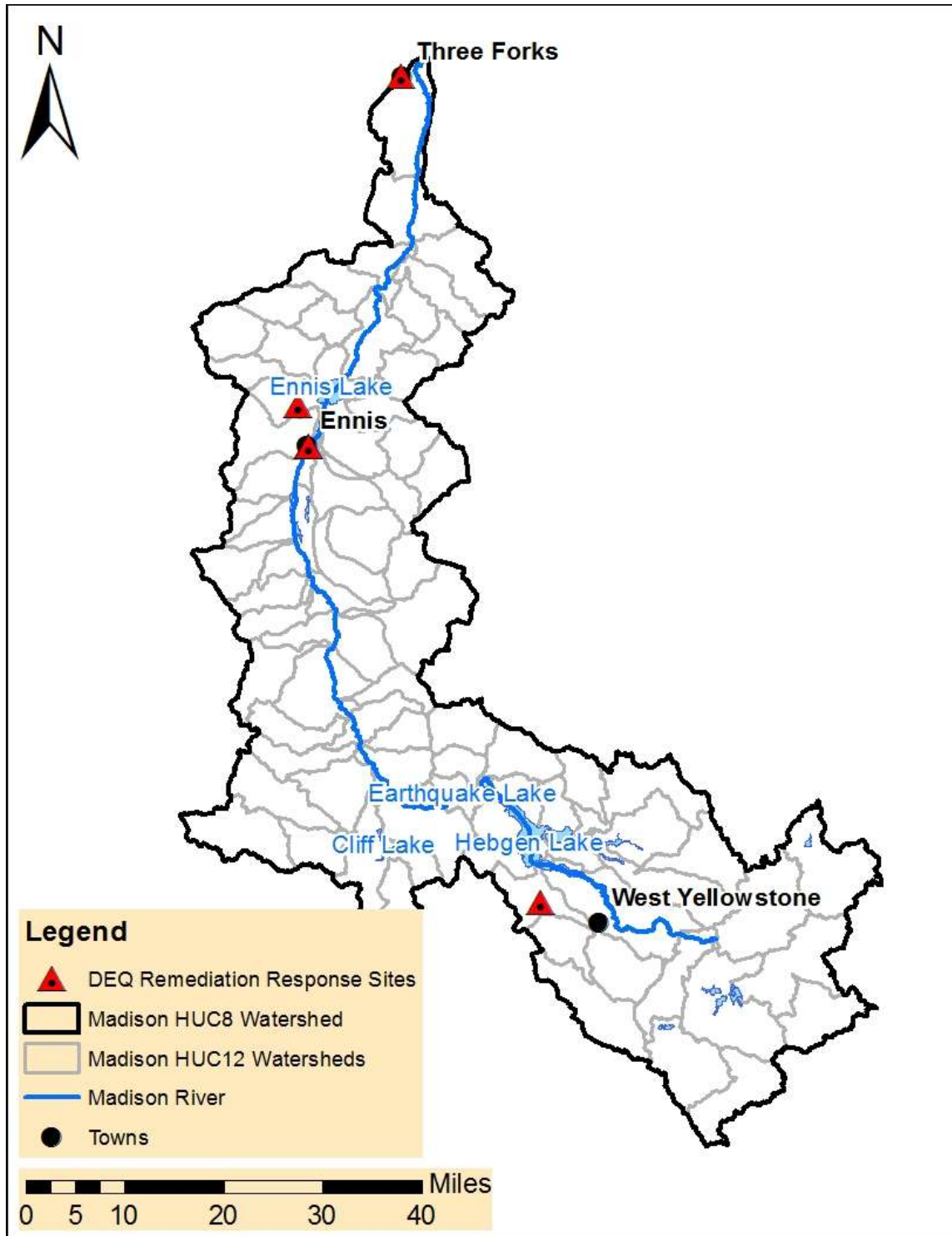


Figure 4-5. DEQ Remediation Response Sites in Madison Basin.

4.3 RUNOFF

4.3.1 Agriculture

As irrigation water percolates through soil it has the potential to cause migration of contaminants that may be present in the soils into local surface waters. Also, water that is diverted from one surface water source may be used in a location that drains to a different surface water source thereby potentially migrating contaminants from the source surface water into a different surface water. **Figure 4-6** shows the DNRC water rights source and use locations for all surface water irrigation rights in the Madison Basin. The Madison River has higher documented arsenic concentrations than its tributaries or ground water in the watershed, therefore any return flow into the Madison River from irrigated lands that use tributary water or ground water will only act to dilute the arsenic concentration in the Madison River.

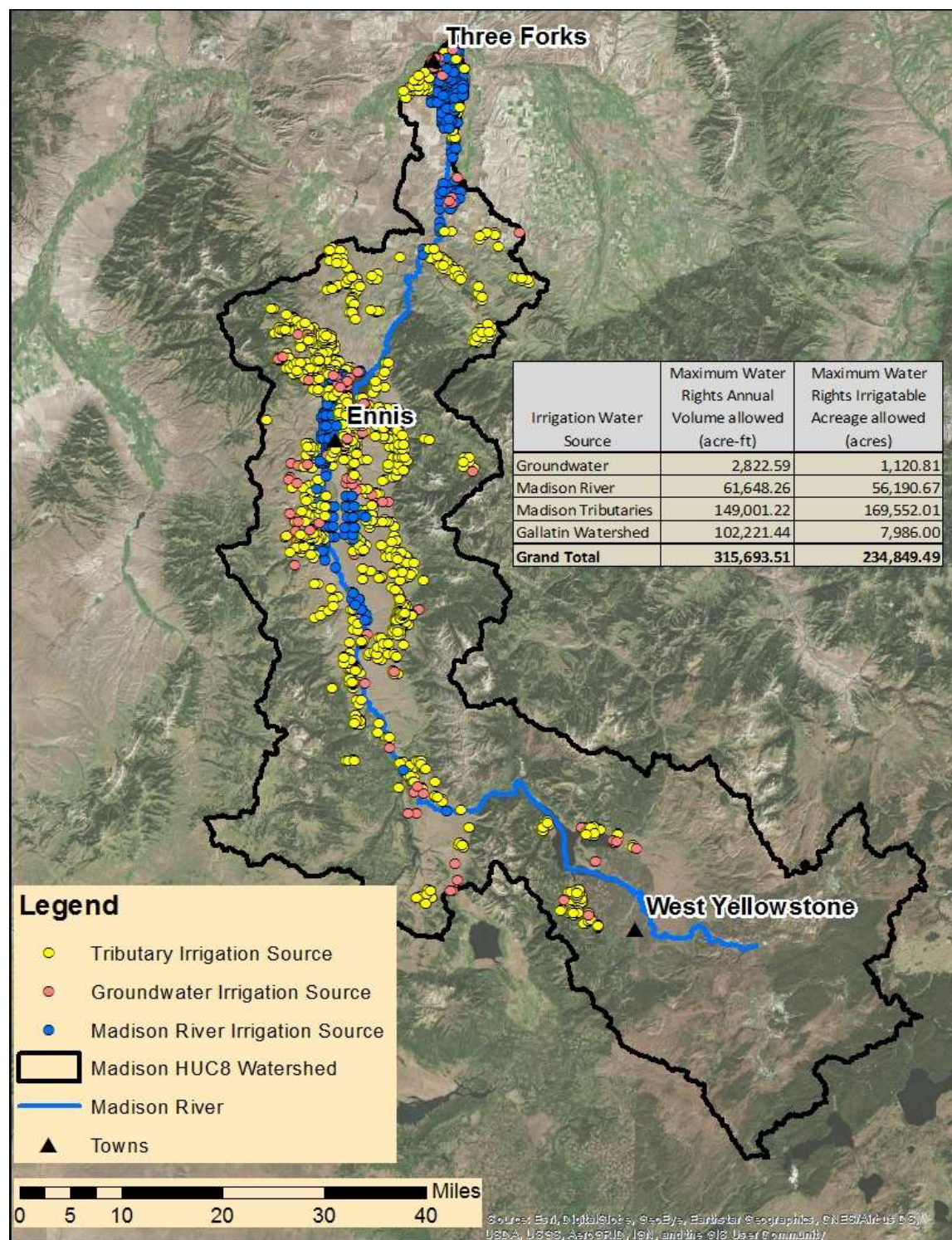


Figure 4-6. DNRC's Water Rights Source and Use Locations for Irrigation Rights

4.3.2 STEPL Modeling

A map showing the soil arsenic concentrations for each Madison Basin HUC12 extrapolated from USGS data is shown in **Figure 4-7** (Smith et al., 2014). The soil concentrations were used to estimate sediment load runoff in the individual HUC12's using the STEPL model as shown in **Figure 4-8**. The resulting STEPL sediment load estimate is an annual load of arsenic runoff. To convert the annual load into a monthly load, the annual load was divided by the monthly percent of annual precipitation from the National Climatic Data Center weather station in Ennis, station number 242793 (1981-2010). This correlation assumes that runoff from land uses is proportional to precipitation, which is a reasonable estimation when the ground is not frozen or covered with snow. Higher elevations of the basin have longer periods of snow coverage, but because most of the anthropogenic land uses are closer to the valley floor, excluding snow cover in the analysis does not produce a significant error.

An annual summary of the STEPL estimate of arsenic load from the land uses showing the difference between the anthropogenic and natural conditions is presented in **Table 4-2**. The annual anthropogenic arsenic load in the last column of **Table 4-2** is the ROA component of the Mass Balance Equation (**Section 2.4**). The monthly anthropogenic arsenic loads from runoff (ROA) to the three hydrologic sections of the Madison River are presented in **Table 4-3**. STEPL spreadsheets are located in Appendix A and an electronic version is available upon request.

The anthropogenic contribution from runoff is less than 0.1% of the total arsenic in the Madison River for all months and all three reaches. Although the load is not significant, the runoff loads will be used in the mass balance equation to calculate the nonanthropogenic load.

As a check for STEPL accuracy and reproducibility using other modeling techniques, STEPL results have been compared to a more comprehensive and calibrated Soil and Water Assessment Tool (SWAT) model for a different DEQ Western Montana modeling project. The Flint Creek Basin has a higher percentage of cropland than the Madison Basin (8.3% versus 2.2%) and a higher percentage of developed (e.g. residential, commercial, roads) land (1.5% versus 0.7%). The sediment loading in the Flint Creek Basin was 0.00074 tons/month/acre while the sediment loading in the Madison Basin is less than half (0.000312 tons/month/acre). The higher loading in Flint Creek resulted from the different percentages of developed land uses. The different model comparison indicate that the STEPL model does a relatively good job of estimating sediment loading compared to the more complex and accurate SWAT model.

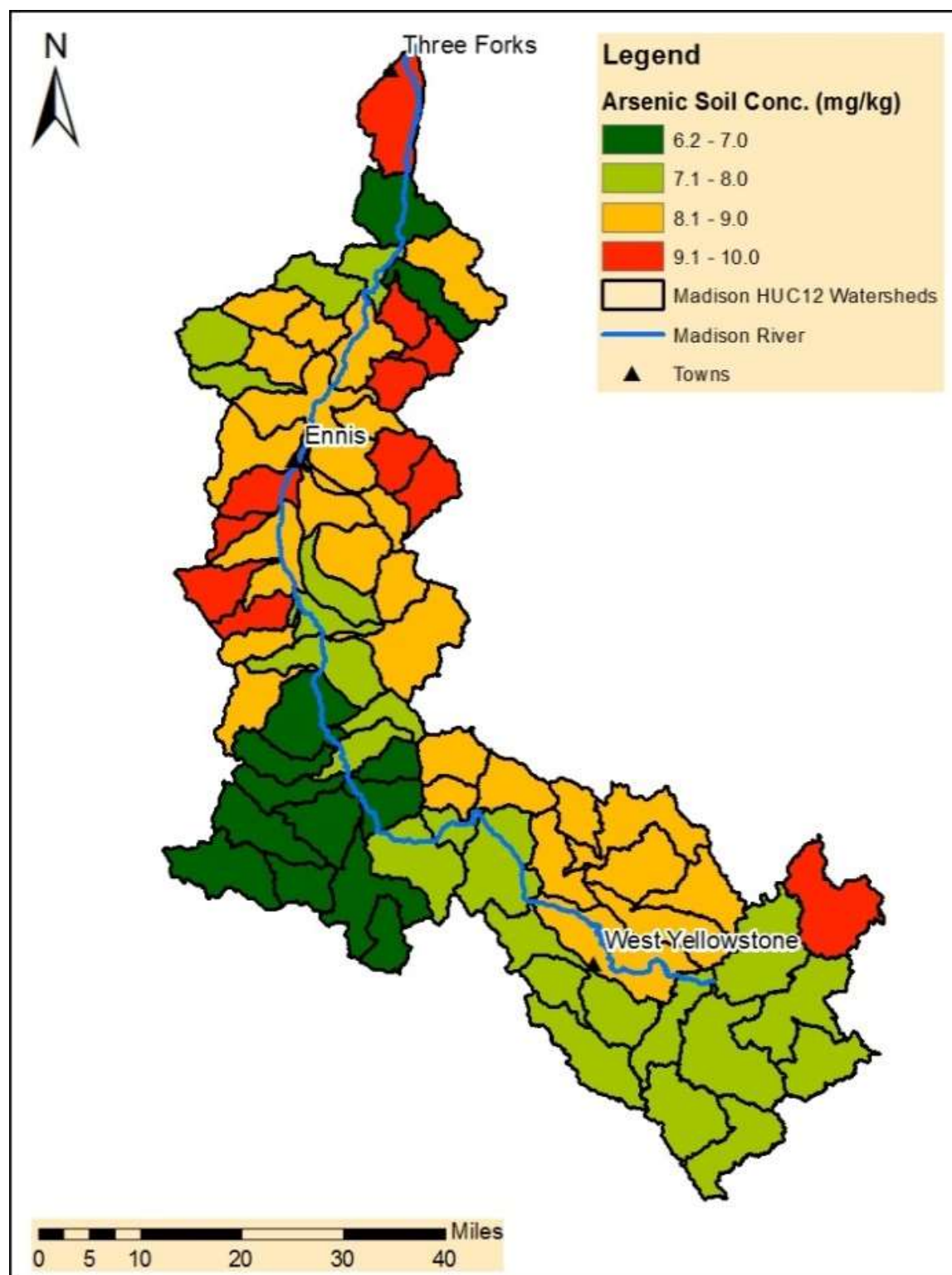


Figure 4-7. Extrapolated Soil Arsenic Concentrations For the Madison River (Smith et al., 2014)

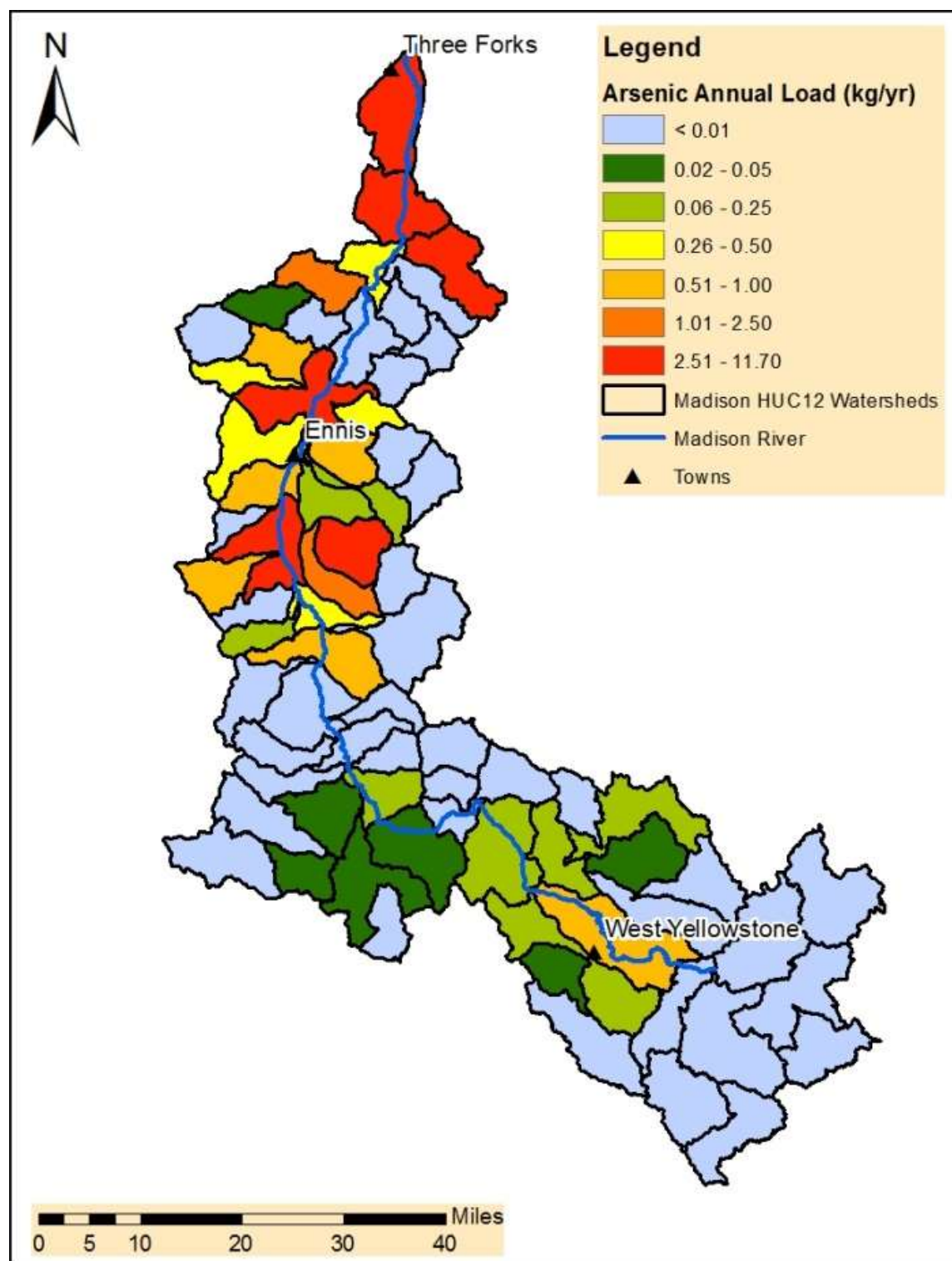


Figure 4-8. Arsenic Loads from STEPL Model for Madison Basin

Table 4-2. STEPL Annual Estimate of Arsenic Runoff from Land Uses Due to Anthropogenic Effects

| Region | STEPL Anthropogenic (Existing Condition) Sediment Load (t/yr) | STEPL Natural Condition Sediment Load (t/yr) | STEPL Sediment Load Due to Anthropogenic Land Uses (t/yr) ¹ | Annual Anthropogenic Arsenic Load (kg/yr) ² |
|--------------------------------------------------|---------------------------------------------------------------|----------------------------------------------|------------------------------------------------------------------------|--------------------------------------------------------|
| Madison West Yellowstone to Madison below Hebgen | 1,520.2 | 1,350.3 | 169.8 | 1.266 |
| Madison below Hebgen to Madison below Ennis Lake | 8,034.9 | 5,682.6 | 2,352.3 | 17.70 |
| Madison below Ennis Lake to Mouth of Madison | 6,615.0 | 3,012.9 | 3,602.1 | 27.27 |
| TOTAL | 16,170.1 | 10,045.9 | 6,124.2 | 46.23 |

¹Calculated by subtracting natural condition load from existing condition load

²Calculated by using average soil concentrations for each HUC12 multiplied by the sediment load due to anthropogenic conditions

Table 4-3. Anthropogenic Arsenic Contribution to Madison River from Runoff (ROA)

| Month | West Yellowstone to below Hebgen | | Below Hebgen to Below Ennis | | Below Ennis to Mouth | |
|------------------|----------------------------------|---------------|-----------------------------|---------------|----------------------|---------------|
| | kg/month | %* | kg/month | %* | kg/month | %* |
| <i>October</i> | 0.10 | 0.001% | 1.38 | 0.018% | 2.12 | 0.030% |
| <i>November</i> | 0.07 | 0.001% | 0.91 | 0.011% | 1.41 | 0.019% |
| <i>December</i> | 0.05 | 0.001% | 0.66 | 0.006% | 1.02 | 0.012% |
| <i>January</i> | 0.04 | 0.001% | 0.60 | 0.005% | 0.92 | 0.010% |
| <i>February</i> | 0.04 | 0.001% | 0.61 | 0.006% | 0.94 | 0.010% |
| <i>March</i> | 0.08 | 0.001% | 1.07 | 0.010% | 1.65 | 0.016% |
| <i>April</i> | 0.13 | 0.002% | 1.87 | 0.018% | 2.88 | 0.031% |
| <i>May</i> | 0.20 | 0.002% | 2.86 | 0.028% | 4.41 | 0.039% |
| <i>June</i> | 0.23 | 0.003% | 3.17 | 0.033% | 4.88 | 0.039% |
| <i>July</i> | 0.12 | 0.002% | 1.66 | 0.021% | 2.55 | 0.031% |
| <i>August</i> | 0.12 | 0.002% | 1.63 | 0.022% | 2.51 | 0.038% |
| <i>September</i> | 0.09 | 0.001% | 1.28 | 0.018% | 1.98 | 0.032% |
| kg/year | | | | | | |
| <i>Annual</i> | <i>1.27</i> | <i>0.001%</i> | <i>17.70</i> | <i>0.016%</i> | <i>27.27</i> | <i>0.026%</i> |

*Percent of total arsenic in the Madison River

4.4 GROUNDWATER

Groundwater concentrations of arsenic in the Madison Basin are shown in **Figure 4-9** (DEQ, 2016d). The highest concentrations are near Three Forks, Montana. The aerial photographs of this area show a very flat terrain with floodplain side channels of the Madison River and the Darlington ditches associated with the Madison River. The groundwater concentrations in this area near Three Forks are very similar to the concentrations measured in the Madison River at Three Forks. The groundwater is likely connected with the nearby Madison River, associated irrigation ditches, and floodplain side channels explaining the higher groundwater arsenic concentrations. For the rest of the Madison Basin, groundwater concentrations are less than Madison River concentrations and if the Madison River gains from groundwater during various times of the year, the groundwater would dilute the arsenic concentration in the Madison River.

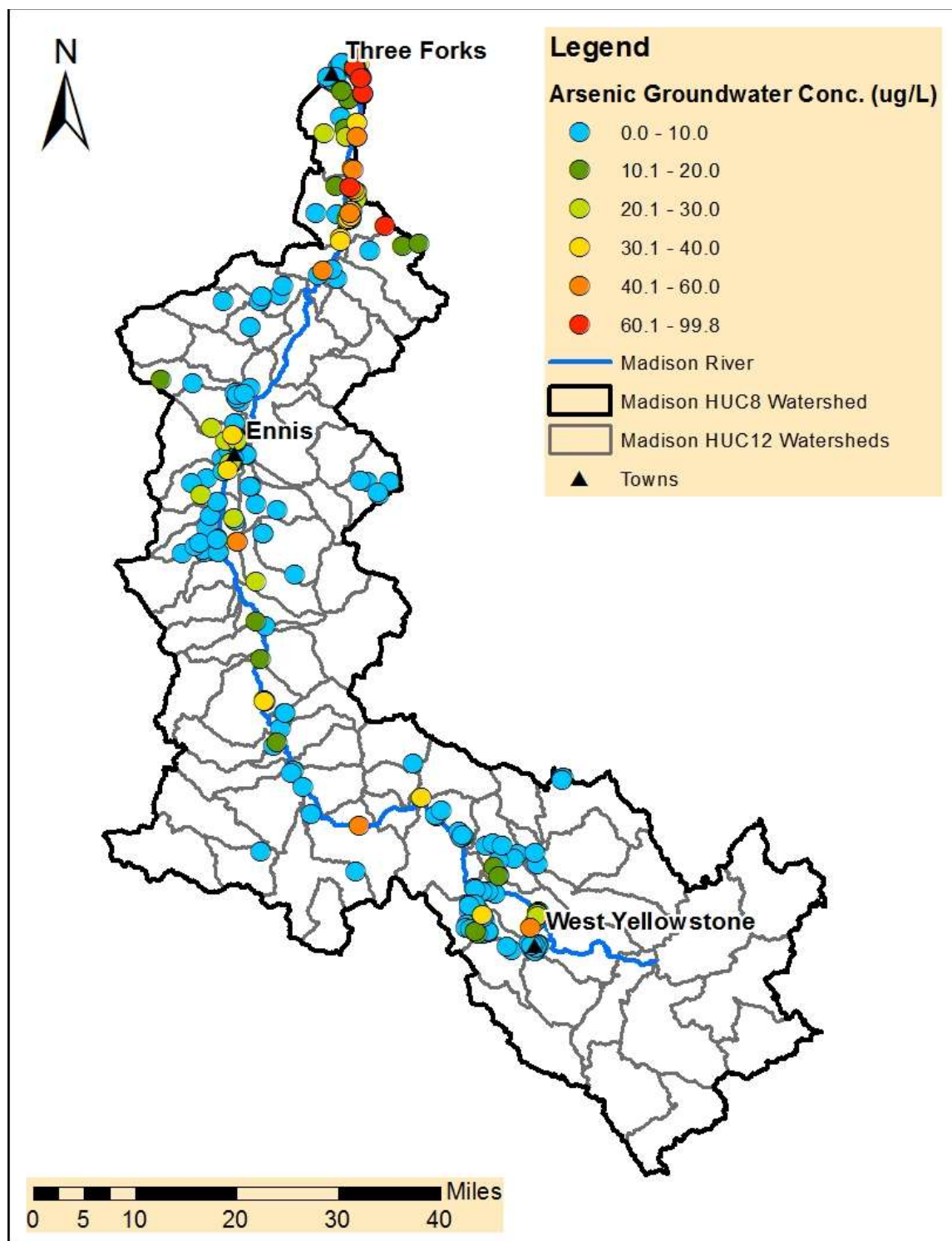


Figure 4-9. Groundwater Arsenic Concentrations in Madison Basin (DEQ, 2016d)

4.5 TRIBUTARIES

Major tributaries were determined based on their low flow volumes (defined as flows from August through April). Many of the tributaries had existing USGS flow gages or had been gaged for a historic period of record. The tributaries that were considered major had average low flow volumes greater than 50 cfs which is roughly 5 percent of the median low flow volume of the Madison River at the mouth. The major tributaries to the Madison River are the Madison River South Fork, Madison River West Fork, Blaine Spring Creek, and O'Dell Creek.

At least 12 paired flow and concentration samples were collected near the mouth of the major tributaries with seasonal and annual representation. All the major tributaries had USGS gages. The data was used for total mass load analysis using the methodologies described in **Section 2.3.2**. The anthropogenic contribution to the Madison River from the tributaries is captured in the runoff loads. The anthropogenic arsenic loads from runoff events flow directly into the mainstem or into tributaries that eventually flow into the Madison River.

There was some question within the Ennis valley as to whether Blaine Spring Creek was contributing a load of arsenic that may have an anthropogenic component not accounted for in runoff or point source loads. The aerial photos of Blaine Spring Creek, between the Alton Ranch and the Arvanites Ranch (where the arsenic load increases drastically), show a braid of the Madison River joining Blaine Spring Creek. For all practical purposes the mass from Blaine Spring Creek is accounted for prior to the Alton Ranch and the additional mass load after Alton ranch is from the Madison River and accounted for in the total arsenic load of the Madison River.

Not all minor tributaries in the Madison were measured for flow or concentration. These tributaries either (1) had no historical record and there was no evidence to suggest they had a potential anthropogenic source or (2) may not have been sampled due to private land access issues or because their contributing area was so small that it was impractical to sample them. Tributaries that were directly measured are shown in **Figure 4-10**. The total Madison River Basin size is 2,554 square miles. The total accounted for area (i.e. tributary contributions that were directly measured) is 1,816 square miles and the unaccounted for area with limited or no data is 738 square miles, or approximately 29 percent of the total area as shown in **Table 4-4** and **Figure 4-10**.

Unaccounted for drainages still contribute total arsenic load to the Madison River and were included in the mass balance. For each of the locations on the Madison River in **Table 4-4**, a ratio of unaccounted for and accounted for drainage area was developed. This ratio was then multiplied by the total arsenic load contribution of the accounted for drainages within the three Madison segments to provide an arsenic load estimate for the unaccounted for drainages. Since the accounted for and unaccounted for area within the Madison have similar physiographic, land use, and geologic conditions, this ratio method can provide a reliable estimate for the total arsenic load from the tributaries that have no arsenic data.

Tributary load calculations were based on presumed high and low flow conditions and the median concentrations of those flow conditions. In this area, high flow conditions were defined as those occurring from May through July, and low flow condition as those occurring from August through April. Many of the tributaries have non-detectable arsenic concentrations and the arsenic load for these drainages was calculated using one half of the laboratory detection limit. The calculations are located in Appendix B.

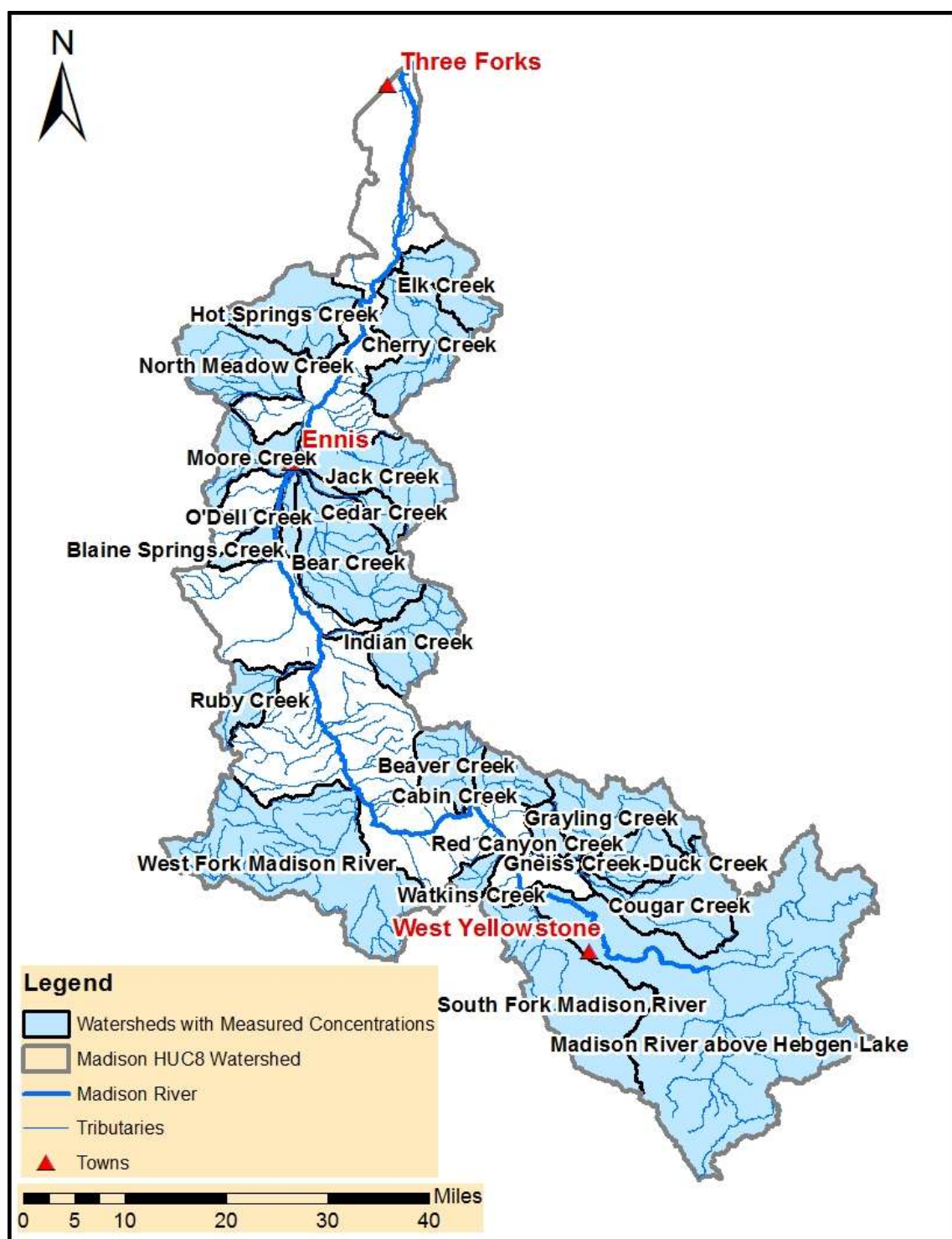


Figure 4-10. Tributaries to the Madison River and Their Associated Drainage Areas

Table 4-4. Accounted and Unaccounted for Drainage Area in the Madison Basin

| Location | Accounted for Area (mile ²) | Unaccounted for Area (mile ²) | Ratio of Unaccounted/Accounted | % of Drainage Area Unaccounted |
|---------------------------------|-----------------------------------------|-------------------------------------------|--------------------------------|--------------------------------|
| USGS near West Yellowstone | 452 | 0 | 0 | 0% |
| USGS below Hebgen near Grayling | 413 | 66 | 0.16 | 14% |
| USGS below Ennis Lake | 750 | 528 | 0.70 | 41% |
| Madison River mouth | 200 | 144 | 0.72 | 42% |
| Total for Madison Basin | 1816 | 738 | 0.41 | 29% |

The total arsenic load contribution from all the tributaries is shown on a monthly basis in **Table 4-5**. The total arsenic load includes both anthropogenic (TribA) and nonanthropogenic sources (TribN). The STEPL arsenic load analysis from sediment runoff estimates includes the anthropogenic land use input for all the tributaries in the Madison Basin. Therefore, the tributary anthropogenic input (TribA) is included in the ROA values presented in **Table 4-3**.

Table 4-5. Total Arsenic Load Contribution to Madison River from Tributaries

| Month | West Yellowstone to below Hebgen | | Below Hebgen to Below Ennis | | Below Ennis to Mouth | |
|------------------|----------------------------------|-------|-----------------------------|-------|----------------------|-------|
| | kg/month | %* | kg/month | %* | kg/month | %* |
| <i>October</i> | 6.0 | 0.08% | 235.0 | 3.08% | 5.4 | 0.08% |
| <i>November</i> | 6.0 | 0.08% | 235.0 | 2.76% | 5.4 | 0.07% |
| <i>December</i> | 6.0 | 0.07% | 235.0 | 2.28% | 5.4 | 0.06% |
| <i>January</i> | 6.0 | 0.07% | 235.0 | 2.01% | 5.4 | 0.06% |
| <i>February</i> | 6.0 | 0.08% | 235.0 | 2.24% | 5.4 | 0.06% |
| <i>March</i> | 6.0 | 0.07% | 235.0 | 2.17% | 5.4 | 0.05% |
| <i>April</i> | 6.0 | 0.07% | 235.0 | 2.29% | 5.4 | 0.06% |
| <i>May</i> | 18.4 | 0.17% | 356.8 | 3.47% | 25.2 | 0.23% |
| <i>June</i> | 18.4 | 0.21% | 356.8 | 3.71% | 25.2 | 0.20% |
| <i>July</i> | 18.4 | 0.24% | 356.8 | 4.46% | 25.2 | 0.31% |
| <i>August</i> | 6.0 | 0.08% | 235.0 | 3.20% | 5.4 | 0.08% |
| <i>September</i> | 6.0 | 0.09% | 235.0 | 3.29% | 5.4 | 0.09% |
| kg/year | | | | | | |
| <i>Annual</i> | 109.5 | 0.11% | 3,185.6 | 2.84% | 124.0 | 0.09% |

*Percent of total arsenic in the Madison River

The tributary arsenic load is assumed to be mainly nonanthropogenic as evidenced in the Mass Balance results (**Section 4.7**). The nonanthropogenic arsenic in this area is associated with groundwater springs and geological formations containing arsenic. The majority of tributary arsenic load originates in the area between Hebgen and Ennis Lake (**Table 4-5**); however, annually is still less than 3% of the total arsenic load in the Madison River. Since the tributary arsenic load is such a small percentage of the total

arsenic in the Madison River, accounting for every arsenic contribution of all Madison basin tributaries is not necessary. The method of estimating arsenic tributary loads (**Table 4-4**) of unaccounted for drainages is acceptable for the Madison Basin since it is unlikely that any one tributary would contribute a significant arsenic load to the Madison River.

4.6 LOADEST MODELING

The total arsenic loads were modeled for three USGS stations on the Madison River and are listed in **Table 4-6**. Each station represents a hydrologic section of the Madison River, as described in **Section 4.1**.

Table 4-6. Madison River Stations Modeled using LOADEST

| USGS ID | Station Description | Latitude | Longitude | Data Years | # Data (n) |
|---------|------------------------------------------------|-----------|-------------|-------------|------------|
| 6037500 | Madison River near West Yellowstone | 44.657072 | -111.067964 | 1995 - 2015 | 105 |
| 6038500 | Madison River below Hebgen Lake near Grayling | 44.866392 | -111.338781 | 1995 - 2015 | 112 |
| 6041000 | Madison River below Ennis Lake near McAllister | 45.490231 | -111.634506 | 1997 - 2015 | 101 |

The input files include daily flow data and synoptic concentration data from 1995 to 2015. For each station there are greater than 100 concentration data points. The model only requires a minimum of 12 concentration data points to calibrate.

Three modeling statistics are presented in **Table 4-7**; absolute relative error, Nash-Sutcliffe model efficiency coefficient (NSE) and the coefficient of determination (R^2). The absolute relative error is the absolute error divided by the magnitude of the exact value. In other words it measures the relative error between the simulated and observed time series. The Nash-Sutcliffe model efficiency coefficient (NSE) is a measure of how well the plot of observed versus simulated data fits a 1:1 line. The closer the NSE is to 1, the better the fit. R^2 is a statistical measure of how close the data are to the fitted regression line and measures how well the regression line approximates the real data points; for example, an R^2 value of 0.68 for the Madison River near West Yellowstone indicates that 68% of the variation in arsenic load is explained by the regression with streamflow. Similar to the NSE, the closer the R^2 to 1, the better the approximation. There is no standard for a good R^2 value. The R^2 value is consistent for all three hydrologic segments suggesting there is similar variance in the data for all three segments. Based on acceptable ranges used by the USGS (Anderson and Rounds, 2010), the modeling statistics are acceptable for all three stations.

Table 4-7. LOADEST Arsenic Load Model Run Statistics

| Station | Mean Absolute Relative Error % | NSE | R^2 |
|------------------------------------------------|--------------------------------|-----------|-----------|
| Madison River near West Yellowstone | 9.03 | 0.68 | 0.68 |
| Madison River below Hebgen Lake near Grayling | 14.61 | 0.69 | 0.69 |
| Madison River below Ennis Lake near McAllister | 17.28 | 0.70 | 0.71 |
| USGS Acceptable Range | 0 - 50 | 0.6 - 1.0 | 0.6 - 1.0 |

Model output files are located in Appendix C. The model outputs daily and monthly loads with estimated concentration data. A summary of the monthly modeled loads is shown in **Figure 4-11**. The monthly results are also listed in **Table 4-8**. These monthly loads are the median of the model estimated loads and include both anthropogenic and nonanthropogenic sources of arsenic.

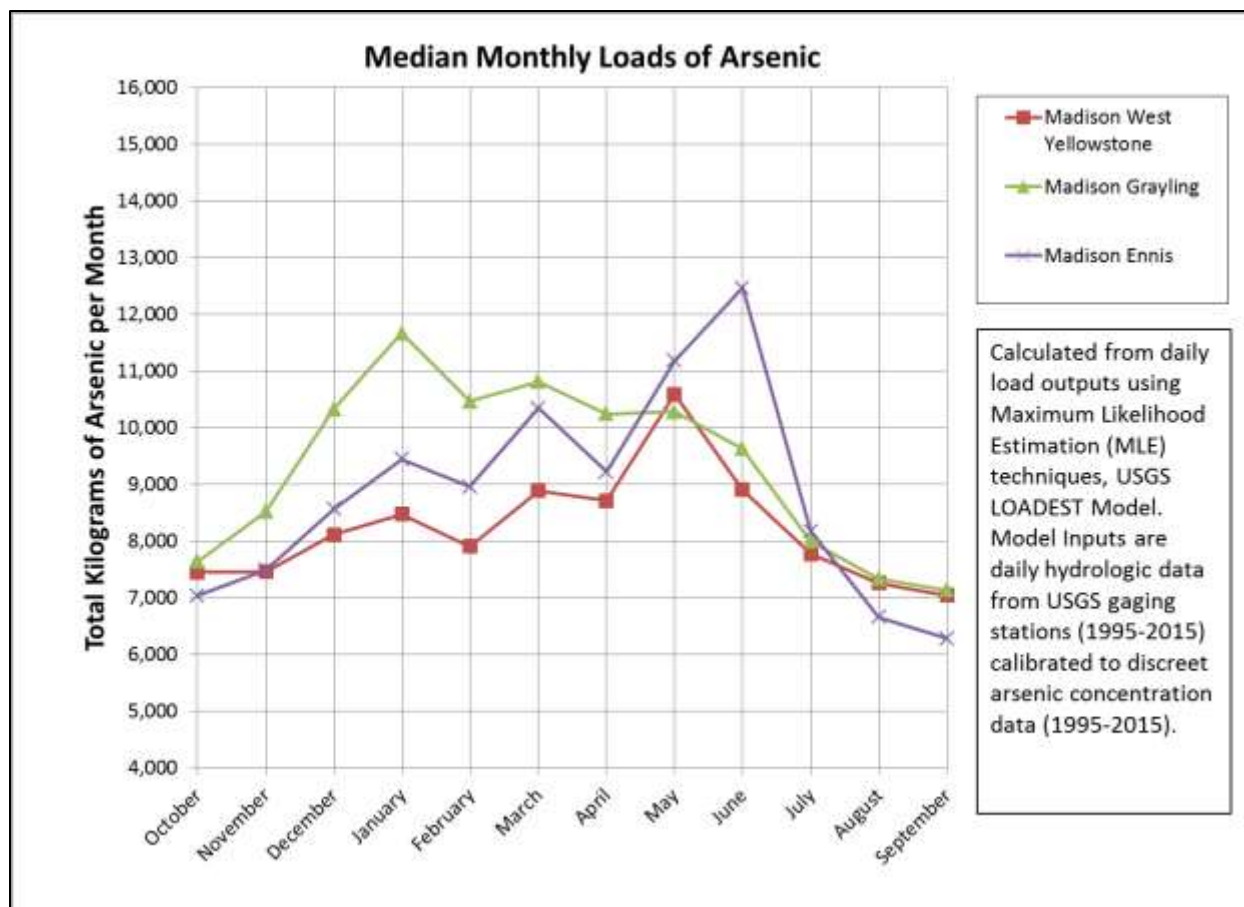


Figure 4-11. LOADEST Output of Median Monthly Arsenic Load

Table 4-8. LOADEST Estimated Median Monthly Arsenic Load

| <i>Month</i> | Madison River near West Yellowstone | Madison River below Hebgen Lake near Grayling | Madison River below Ennis Lake near McAllister |
|------------------|------------------------------------------------|--------------------------------------------------------------|---------------------------------------------------------------|
| <i>kg/month</i> | | | |
| <i>October</i> | 7,454 | 7,642 | 7,037 |
| <i>November</i> | 7,462 | 8,522 | 7,493 |
| <i>December</i> | 8,116 | 10,327 | 8,564 |
| <i>January</i> | 8,477 | 11,670 | 9,444 |
| <i>February</i> | 7,909 | 10,471 | 8,960 |
| <i>March</i> | 8,891 | 10,817 | 10,342 |
| <i>April</i> | 8,712 | 10,246 | 9,220 |
| <i>May</i> | 10,591 | 10,285 | 11,185 |
| <i>June</i> | 8,905 | 9,625 | 12,465 |
| <i>July</i> | 7,773 | 7,998 | 8,171 |
| <i>August</i> | 7,259 | 7,336 | 6,661 |
| <i>September</i> | 7,047 | 7,134 | 6,279 |
| <i>kg/year</i> | | | |
| <i>Annual</i> | 98,596 | 112,074 | 105,821 |

4.7 MASS BALANCE RESULTS

The modeling results and other calculated anthropogenic and nonanthropogenic loads were used in the mass balance equations. The mass balance equation is used to calculate the final nonanthropogenic condition of the Madison River. The mass balance equation that defines the Nonanthropogenic Arsenic Load (NAL) is shown in **Equation 7**.

EQUATION 7:
$$\text{NAL} = \text{TAL} - \text{PSL} - \text{GWA} - \text{TribA} - \text{ROA}$$

The mass balance results are presented using the median monthly results of nonanthropogenic and anthropogenic loads. The monthly total arsenic loads (TAL), point source loads (PSL), and anthropogenic run off loads (ROA) were calculated in previous sections and are used in the equation to calculate NAL. As discussed in previous sections, the anthropogenic tributary load (TribA) is accounted for in the ROA and the groundwater anthropogenic contribution (GWA) is assumed to be zero. Therefore, the equation is rewritten and presented as **Equation 8**.

EQUATION 8:
$$\text{NAL} = \text{TAL} - \text{PSL} - \text{ROA}$$

The median monthly NAL is presented in **Table 4-9**. An annual summary for the three stations is presented in **Table 4-10**.

Table 4-9. Median Monthly Arsenic Load Summary for Madison River

| <i>Month</i> | Median Total Arsenic Load (TAL) | Point Source Load (PSL) | Anthropogenic Runoff Load (ROA) | Median Nonanthropogenic Loads (NAL) |
|--------------------------------------------------------------|----------------------------------------|--------------------------------|----------------------------------------|--------------------------------------------|
| <i>West Yellowstone to Below Hebgen Lake (kg/day)</i> | | | | |
| <i>October</i> | 7,453.9 | 0.0 | 0.10 | 7,453.8 |
| <i>November</i> | 7,462.3 | 0.0 | 0.07 | 7,462.2 |
| <i>December</i> | 8,116.1 | 0.0 | 0.05 | 8,116.1 |
| <i>January</i> | 8,477.3 | 0.0 | 0.04 | 8,477.3 |
| <i>February</i> | 7,908.6 | 0.0 | 0.04 | 7,908.5 |
| <i>March</i> | 8,890.7 | 0.0 | 0.08 | 8,890.6 |
| <i>April</i> | 8,711.6 | 0.0 | 0.13 | 8,711.4 |
| <i>May</i> | 10,591.3 | 0.0 | 0.21 | 10,591.1 |
| <i>June</i> | 8,904.5 | 0.0 | 0.23 | 8,904.3 |
| <i>July</i> | 7,772.9 | 0.0 | 0.12 | 7,772.8 |
| <i>August</i> | 7,259.4 | 0.0 | 0.12 | 7,259.3 |
| <i>September</i> | 7,047.0 | 0.0 | 0.09 | 7,046.9 |
| <i>Below Hebgen Lake to Below Ennis Lake (kg/day)</i> | | | | |
| <i>October</i> | 7,641.9 | 3.2 | 1.4 | 7,637.3 |
| <i>November</i> | 8,522.2 | 3.2 | 0.9 | 8,518.1 |
| <i>December</i> | 10,327.4 | 3.2 | 0.7 | 10,323.6 |
| <i>January</i> | 11,669.5 | 3.2 | 0.6 | 11,665.7 |
| <i>February</i> | 10,470.6 | 3.2 | 0.6 | 10,466.8 |
| <i>March</i> | 10,817.4 | 3.2 | 1.1 | 10,813.1 |
| <i>April</i> | 10,246.4 | 3.2 | 1.9 | 10,241.2 |
| <i>May</i> | 10,285.4 | 3.2 | 2.9 | 10,279.2 |
| <i>June</i> | 9,625.1 | 3.2 | 3.2 | 9,618.6 |
| <i>July</i> | 7,998.3 | 3.2 | 1.7 | 7,993.3 |
| <i>August</i> | 7,335.8 | 3.2 | 1.6 | 7,330.9 |
| <i>September</i> | 7,133.8 | 3.2 | 1.3 | 7,129.3 |
| <i>Below Ennis Lake to Mouth of Madison River</i> | | | | |
| <i>October</i> | 7,029.7 | 0.5 | 2.1 | 7,637.3 |
| <i>November</i> | 7,487.5 | 0.5 | 1.4 | 8,518.1 |
| <i>December</i> | 8,558.4 | 0.5 | 1.0 | 10,323.6 |
| <i>January</i> | 9,439.0 | 0.5 | 0.9 | 11,665.7 |
| <i>February</i> | 8,955.0 | 0.5 | 0.9 | 10,466.8 |
| <i>March</i> | 10,335.4 | 0.5 | 1.7 | 10,813.1 |
| <i>April</i> | 9,211.1 | 0.5 | 2.9 | 10,241.2 |
| <i>May</i> | 11,173.1 | 1.3 | 4.4 | 10,279.2 |
| <i>June</i> | 12,451.9 | 1.3 | 4.9 | 9,618.6 |
| <i>July</i> | 8,162.5 | 1.3 | 2.6 | 7,993.3 |
| <i>August</i> | 6,652.7 | 0.5 | 2.5 | 7,330.9 |
| <i>September</i> | 6,272.3 | 0.5 | 2.0 | 7,129.3 |

Table 4-10. Median Annual Arsenic Load Summary for Madison River

| Station | Median Total Arsenic Load (TAL) | Point Source Load (PSL) | Anthropogenic Runoff Load (ROA) | Nonanthropogenic Loads (NAL) |
|---------------------------------------|---------------------------------|-------------------------|---------------------------------|------------------------------|
| kg/year | | | | |
| West Yellowstone to Below Hebgen Lake | 98,595.5 | 0.00 | 1.27 | 98,594.3 |
| Below Hebgen Lake to Below Ennis Lake | 112,073.7 | 37.9 | 17.7 | 112,016.8 |
| Below Ennis Lake to Mouth of Missouri | 105,820.6 | 7.8 | 27.3 | 105,728.7 |

5.0 CONCLUSIONS

The arsenic mass balance for the Madison River is summarized in **Table 5-1**. The anthropogenic arsenic load at West Yellowstone is assumed to be zero due to the Madison River watershed being entirely contained within Yellowstone National Park above this point. From West Yellowstone to the mouth of the Madison River, the Madison River accumulates 92 kg/year of anthropogenic arsenic, only 0.1 percent of the total arsenic load, and 7,133 kg/year of nonanthropogenic arsenic, only 6.8 percent of the total arsenic load. Forty six percent (3,327 kg/year) of the net gain is attributed to tributary nonanthropogenic arsenic. The remaining increase of nonanthropogenic arsenic (3,807 kg/year) is only 4 percent of the total nonanthropogenic arsenic at the mouth of the Madison River. The source of this small unaccounted for nonanthropogenic arsenic load is likely either groundwater contribution from gaining reaches and/or error associated with mass balance calculations.

Table 5- 1. Mass Balance and Nonanthropogenic Load Summary

| Parameter | West Yellowstone | | Mouth of Madison | | Change from West Yellowstone to Mouth | |
|----------------------------------------------------------------------------------------------|------------------|-----------------------------------------------------|------------------|-----------------------------------------------------|---------------------------------------|--------|
| | Load (kg/yr) | % of Total Arsenic Load at the Mouth of the Madison | Load (kg/yr) | % of Total Arsenic Load at the Mouth of the Madison | Load (kg/yr) | % |
| Total Arsenic Load | 98,596 | 93.2% | 105,821 | 100.0% | 7,225 | 6.8% |
| Anthropogenic Arsenic Load | 0 | 0.0% | 92 | 0.1% | 92 | 100.0% |
| Natural Arsenic Load | 98,596 | 93.2% | 105,729 | 99.9% | 7,133 | 6.7% |
| Natural Tributary Load | 0 | 0.0% | 3,327 | 3.1% | 3,327 | 100.0% |
| Unaccounted for Natural Load (groundwater contribution plus mass balance calculation errors) | | | 3,806 | 3.6% | | |
| Known Natural Arsenic Load (not including unaccounted for natural load) | | | 101,923 | 96.3% | | |

The original YNP arsenic load is 93 percent of the total arsenic load at the mouth of the Madison River and is the primary source of the elevated arsenic concentrations in the Madison River. Tributary, runoff,

groundwater, and unknown contributions account for the remaining 7 percent of nonanthropogenic arsenic. The nonanthropogenic arsenic is 99.9 percent of the total arsenic load at the mouth of the Madison River. Therefore, the ambient arsenic load of the Madison River is roughly equal to the nonanthropogenic arsenic load with non-significant contributions from anthropogenic sources.

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APPENDICES

A. STEPL SPREADSHEETS

See Electronic File

B. TRIBUTARY LOAD CALCULATIONS

See Electronic File

C. LOADEST MODEL OUTPUT

See Electronic File

D. MASS BALANCE CALCULATIONS

See Electronic File